

Transformations of mercury in processes of solid fuel combustion – review

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Abstract: The paper presents current reports on kinetics and mechanisms of reactions with mercury which take place in the exhaust gases, discharged from the processes of combustion of solid fuels (coals). The three main stages were considered. The first one, when thermal decomposition of Hg components takes place together with formation of elemental mercury (Hg^0). The second one with homogeneous oxidation of Hg^0 to Hg^{2+} by other active components of exhaust gases (e.g. HCl). The third one with heterogeneous reactions of gaseous mercury (the both – elemental and oxidised Hg) and solid particles of fly ash, leading to generation of particulate-bound mercury (Hg_p). Influence of exhaust components and their concentrations, temperature and retention time on the efficiency of mercury oxidation was determined. The issues concerning physical (gas–solid) and chemical speciation of mercury (fractionation Hg^0 – Hg^{2+}) as well as factors which have influence on the mercury speciation in exhaust gases are discussed in detail.

Introduction

Mercury is released into the environment from natural (e.g. volcanic eruptions) and anthropogenic sources. It is estimated that, in a global scale, mercury emitted as a result of human activity constitutes between 30% and 60% of this element's total emission into the environment (Pacyna et al. 2016). These data prove mercury to be a factor of significant detrimental effect on the ecosystem.

A survey of European mercury emission sources, conducted under projects financed by the United Nations Economic Commission for Europe (UNECE) through the Convention on Long-Range Transboundary Air Pollution (LRTAP), the Baltic Marine Environment Protection Commission, also known as Helsinki Commission (HELCOM), and the Oslo and Paris Commissions (OSPAR) for the Protection of the Marine Environment of the North-East Atlantic, has identified solid fuel combustion processes to be the main anthropogenic sources of mercury. It has been established that emission of Hg from commercial power installations accounts for more than 26% (63.5 tonnes) of the total Hg emission in EU countries, whereas uncontrolled emission from processes of fuel combustion in household furnaces is at the level of around 20% (48.8 tonnes) (Pacyna et al. 2006). For comparison, in the USA, it is estimated that 41.6% (48.7 tons per year) of mercury emission into the air is caused by fuel combustion in utility boilers (Praveen 2003).

Due to mercury toxicity, the U.S. Congress placed this element in the 1990 Clean Air Act Amendments (CAAA)

as a hazardous air pollutant. The Clean Air Mercury Rule (CAMR) would have placed the limit values on the mercury emissions from coal-fired power plants; however the U.S. Court of Appeals, District Columbia vacated them in 2008. Final Mercury and Air Toxics Standards (MATS) from coal-fired power plants have been issued by the U.S Environmental Protection Agency (EPA) in 2011 (US EPA 2011, Wilcox et al. 2012). And similarly, in 2006 the Canadian Council of Ministers of the Environment (CCME) endorsed the Canada – wide Standards (CWSs) for the coal-fired electric power generation sector. The CWSs set targeted emissions caps for individual provinces for the year 2010 with the possibility of more stringent reductions by 2018 (CCME, 2006).

The USA and Canada have set stringent emission limits for coal-fired plants which require many plants to install mercury-specific control technologies. Other countries, such as the Member States of the European Union and some countries in Asia (Japan, Korea, China) are taking a less stringent legislative approach based on the mercury co-benefit control technologies, used for reduction of other pollutants emissions (particulate matter PM, sulphur dioxide SO_2 and nitrogen oxides NO_x) (Rallo et al 2012, Sloss 2012).

Because of the diversified properties of individual mercury forms, it is important to determine the speciation of this element. In natural environments mercury exists both in inorganic (Hg^0 , Hg^{2+}) and organic forms (e.g. methylmercury). Individual forms differ considerably from one another in terms of physical and chemical properties (Table 1). Compared to elemental mercury, Hg^{2+} (except for HgS) and organometallic

Table 1. Properties of mercury compounds (adopted from Kabata-Pendias and Pendias 1999)

Parameter	Hg ⁰	HgCl ₂	HgO	HgS	CH ₃ HgCl	(CH ₃) ₂ Hg
Melting point, °C	-39	277	degradation at 500°C	584 (sublimation)	167 (sublimation)	–
Boiling point, °C	357 (1 atm)	303 (1 atm)	–	–	–	96 (1 atm)
Vapor pressure, Pa	0.180 (20°C)	899 × 10 ⁻³ (20°C)	9.20 × 10 ⁻¹² (25°C)	–	1.76 (25°C)	8.30 × 10 ³ (24°C)
Solubility in water, g/dm ³	49.4 × 10 ⁻⁶ (20°C)	66 (20°C)	5.3 × 10 ⁻² (25°C)	~2 × 10 ⁻²⁴ (25°C)	~5–6 (25°C)	2.95 (24°C)
Octanol-water partition coefficient	4.2	0.5	–	–	2.5	180

compounds of mercury are less volatile, more water soluble, and more chemically reactive. The differences in their physical and chemical properties, and particularly the good water solubility of Hg²⁺X, result in more efficient removal of these compounds in conventional flue gas purification systems when compared to the elemental mercury. The knowledge of physical and chemical transformation of mercury in combustion processes allows to select the right method of reduction of mercury emission to the atmosphere and decide whether more appropriate would be application of particulate emission control devices (fabric filters FFs, electrostatic precipitators ESPs) or adsorption methods (in-duct sorbent injection, sorbent bed technologies) or absorption techniques (wet scrubbers with or without additives), etc. (Józewicz 2007, Hlawiczka and Fudala 2008).

The speciation of mercury in flue gases is crucial for reducing its emissions to the atmosphere. The exhaust from coal combustion may contain mercury in a particulate-bound form (Hg_p) as well as in a gaseous elemental (Hg⁰) and oxidized (Hg⁺²) forms, whereas there are no data confirming the presence of organometallic compounds of mercury in flue gas. The predominant form of oxidized mercury in flue gas are halides, mainly HgCl₂ as well as HgBr₂ and HgI₂, occurring in both, the gaseous phase and particulate-bound form. Flue gas may also contain HgO_(g) as well as particulate-bound mercury compounds, such as Hg²⁺X (where X stands for SO₄²⁻, S²⁻, O²⁻) (Praveen 2003, Wilcox et al. 2012). When coal is combusted in low capacity domestic heating units only about 50% of mercury contained in coal is emitted to the air in gaseous form (Hlawiczka et al. 2003). The second half of the mercury is present in particulate matter (Hg_p), partially trapped in chimney duct. Data available in the relevant literature suggest that Hg_p present in ambient air of urban and industrial areas accounts for up to 15% of the total atmospheric mercury (Pyta et al. 2009, Beldowska et al. 2012, Nowak et al. 2013, Nowak et al. 2014).

Mercury content in coals

Mercury exists in coal as inorganic and organic components. However, studies on the determination of Hg in organic matter in coal are quite limited (Kolker et al., 2006). Mercury can be associated with pyrite (FeS₂), sphalerite, and cinnabar (HgS). Sometimes it can occur in a form of elemental (metallic) mercury or in forms bound to coal macerals. The studies conducted by Zheng et al. (2007) indicated that this element was mainly found in the form of sulphides (40% of total Hg

content) and organic matter (30%). Mercury is a chalcophile element, with great affinity to sulphur-containing components, generally incorporated in pyrite (Kolker et al. 2006, Mukherjee et al. 2008). Therefore, the conventional coal cleaning process may be an effective method of removing the substantial amounts of Hg as it occurs in coarse-grained pyrite (Finkelman, 1994).

Mercury is a coal micro-component. The average Hg content varies significantly for various countries from 0.01 to over 1.0 mg/kg (Table 2). But its higher content (>1.0 mg/kg) is quite rare. There are some coals highly enriched in Hg (and other sulphophile elements such as: As, Se, Pb, Cu, and Zn). Such coals are located in the Donbas (Ukraine), particularly in the Donetsk coal basin, Russian Far East, Southern China, Appalachian basin and Texas (USA) (Toole-O'Neil et al. 1999, Yudovich and Ketris 2005a). Yudovich et al. (2005a) reported that Hg content in Russian Pacific coals was up to 15 mg/kg. The coals from Ukrainian Donbas contained on average 0.12–2.37 mg/kg of mercury, but some samples contained almost 60 mg/kg of mercury (Yudovich et al. 2005a, Wichliński et al. 2013). Such high mercury concentrations were confirmed by Kolker et al. (2009) who reported that the Donbas coals contained 0.02–26 mg/kg of mercury.

Mercury content in coals generally depends on coal density and the presence of sulphur (Mukherjee et al. 2008). When coals have high density, e.g. are buried deep in the ground they often contain a high concentration of Hg. This concerns Korean anthracite coals (Park et al. 2006) and Appalachian bituminous coals (Ruch et al. 1974). Yudovich and Ketris (2005a, 2005b) concluded that there is strong evidence that high-sulphur coals usually contain more Hg, mainly in the pyritic form. In the extremely Hg-enriched Donbas coals, both sulphides (HgS) and metallic mercury (Hg⁰) occur. In low-sulphur coals, which are generally poor in Hg, two Hg forms dominate: organic and sulphide mercury (Yudovich and Ketris 2005a).

Mercury speciation in flue gases

EPA's Information Collection Request (ICR) to coal-burning utilities indicated that on average 60% of Hg entering a power plant is emitted to the air and 40% is captured (Kilgroe et al. 2001). Numerous studies showed that percentage emissions of mercury for individual plants varied widely (from 5% to 90% of Hg entering with coal) depending on the coal composition and conditions of combustion process (Chow et al. 1994, Jones 1994, Galbreath and Zygarlicke 1996, Widmer et al. 1998, Galbreath and Zygarlicke 2000, Sakulpitakphon et al. 2000, Senior et al. 2000, Dunham et al. 2003, Mardon and Hower

Table 2. Content of Hg in coals (adopted from UNEP 2016)

Country (Region)	Coal type	Concentration of Hg, mg/kg		Reference
		Mean	Range	
Australia	Bituminous	0.075	0.01–0.31	Nelson 2007, Tewalt et al. 2010
Argentina	Bituminous	0.19	0.02–0.96	UNEP 2010, Tewalt et al. 2010
Brazil	Bituminous Subbituminous	0.20 0.30	0.04–0.81 0.06–0.94	UNEP 2010, Tewalt et al. 2010
Canada	–	0.058	0.033–0.12	Tewalt et al. 2010
Chile	Bituminous Subbituminous	0.21 0.033	0.03–2.2 0.022–0.057	Tewalt et al. 2010
China	Bitumin./Subbitumin.	0.17	0.01–2.248	Zhang et al. 2012, UNEP 2011
Colombia	Subbituminous	0.069	0.02–0.17	UNEP 2010
Czech Rep.	Lignite Bituminous	0.338 0.126	<0.03–0.79 0.03–0.38	UNEP 2010, Tewalt et al. 2010
Germany	Bituminous Lignite	0.354 0.05	0.7–1.4 Max: 0.09	Pirrone et al. 2001 UNEP 2016
Great Britain	Bituminous	0.216	0.012–0.6	Tewalt et al. 2010
Hungary	Lignite Subbituminous Bituminous	0.242 0.138 0.354	0.075–0.44 0.04–0.31 0.091–1.2	Tewalt et al. 2010
India	Bituminous Lignite	0.106 0.071	0.02–0.86 0.053–0.093	Tewalt et al. 2010, UNEP 2013a
Indonesia	Subbituminous Lignite	0.03 0.11	0.01–0.05 0.02–0.19	US EPA 2002 UNEP 2010, Tewalt et al. 2010
Japan	Bituminous	0.045	0.01–0.21	Ito et al. 2006
Kazakhstan	Bituminous	0.08	<0.03–0.14	Tewalt et al. 2010
New Zealand	Bituminous Subbituminous	0.073 0.082	0.03–0.1 0.062–0.13	Tewalt et al. 2010
Mongolia	Bituminous	0.097	0.02–0.22	Tewalt et al. 2010
Poland	Bituminous Bituminous Lignite Bituminous Lignite	0.085 0.100 0.250 – –	0.013–0.163 0.05–0.150 0.120–0.370 0.013–0.156 0.079–0.230	Bojakowska & Sokołowska 2001 Wojnar & Wisz 2006 Wojnar & Wisz 2006 Wichliński et al. 2013 Wichliński et al. 2013
Romania	Lignite/Subbitumin.	0.21	0.07–0.46	UNEP 2010
Russia	Bitumin./Subbitumin.	0.12	<0.02–0.25	Romanov et al. 2012, UNEP 2013b
Slovak Rep.	Bituminous Lignite	0.08 0.057	0.03–0.13 0.032–0.14	UNEP 2010 Tewalt et al. 2010
South Africa	Bituminous	0.157	0.023–0.1	Leaner et al. 2009, Tewalt et al. 2010
South Korea	Anthracite	0.30	0.02–0.88	UNEP 2010
Tanzania	Bituminous	0.12	0.03–0.22	UNEP 2010
Turkey	Lignite	0.12	0.03–0.66	Tewalt et al. 2010
Ukraine (Donbas): Donetsk-Makeevsky Krasnoarmeevsky Alma-Marievsky Charabowska area	Bituminous	0.99 2.37 0.12 0.88	0.17–3.09 <0.01–6.0 <0.01–8.4 0.40–1.30	Kolker et al. 2009, Wichliński et al. 2013
USA	Subbituminous Lignite Bituminous Anthracite	0.10 0.15 0.21 0.23	0.01–8.0 0.03–1.0 <0.01–3.3 0.16–0.30	US EPA 1997
Vietnam	Anthracite	0.28	<0.02–1.14	UNEP 2010

2004, Lee et al. 2006, Zhao et al. 2006, Lopez-Anton et al. 2010). They also showed that Hg concentrations in stack gases varied in a wide range between 3 and 70 $\mu\text{g}/\text{m}^3$.

Mercury in coal-fired power plants is found mainly as gaseous elemental (Hg^0) and oxidized (Hg^{2+}) form and as particulate mercury (Hg_p) bound with fly ash. Depending on its mode of occurrence, mercury can be captured by different types of air pollution control devices (APCDs). Flue gas composition plays an important role in Hg speciation. As the combustion gases are cooled, homogenous reactions (gas–gas) and heterogeneous interactions with fly ash (gas–solid) occur affecting the mercury oxidation and its removal by APCDs.

ICR data on coal-burning utilities indicated very little mercury removal within pulverized coal-fired (PC) boilers. The level of mercury oxidation at the exit of PC boiler was increased for higher coal chlorine contents and lower flue gas temperatures. Therefore, Hg removals within PC boilers equipped with cold-side ESPs averaged 27%, compared to 4% for hot-side ESPs (Pavlish et al. 2003). Mercury removals for FFs were generally higher than for ESPs, averaging 58%, owing to enhanced heterogeneous Hg oxidation (longer gas–solid contact time) (Cao et al. 2008). Elemental mercury is the most difficult to capture, but selective catalytic reduction units (SCRs) are able to convert elemental mercury to oxidized form allowing it to be subsequently captured by wet flue gas desulphurization systems (FGDs). Both wet and dry FGD systems without SCR removed 80–90% of the oxidized mercury, but elemental mercury was not affected (Pavlish et al. 2003). Only the combination of SCRs and FGDs was considered as an effective Hg control method (Józewicz 2007, Pan et al. 2013).

It has been proved that the content of elemental mercury in total mercury emitted from a 190 MW PC boiler ranged from 30% to 70% when SCR was applied (Wu et al. 2010). Wu and co-authors also highlighted oxidation efficiency reaching 71% in the SCR systems. By means of the wet FGD without SCR, it was possible to capture 54.9–68.8% of total mercury, while with the SCR system the mercury removal efficiencies ranged from 78% to 90.2% (Winberg et al. 2004, Eom et al. 2008, Strege 2008).

Review of ICR data proved high mercury removals, averaging 86%, in fluidized-bed combustors (FBCs) with FFs (Pavlish et al. 2003). This was possible due to efficient mercury capture on high-carbon fly ash. Fly ash structure (the specific surface area) is also essential factor of lower Hg emission rates in the FBC units. The specific surface area of fly ash from the FBCs (on average 15 m^2/g) was generally higher than those from PC boilers (1–10 m^2/g) (Cao et al. 2008). The percentage of Hg^0 in the total Hg emission from the FBCs with fabric filtration was higher than for PC boilers equipped with FFs, averaging 56% versus 23% (Pavlish et al. 2003). This is probably due to the removal of chlorine from flue gas by bed calcium (the limestone in FBC) before it can promote the oxidation of mercury.

Basic parameters which affect chemical and physical speciation of mercury are the process temperature, the content of chlorine, sulphur, iron, and calcium in coals as well as the concentration of HCl and ammonia in flue gas (Sliger et al. 2000, Pavlish et al. 2003, Zhuang et al. 2004, Lee et al. 2006, Zhao et al. 2006). It is estimated that more than 85% of the mercury in flue gas from combustion of coal with low-chlorine

content ($\text{Cl} < 150$ ppm) represents elemental mercury. An opposite trend may be observed in combustion of the coals of chlorine content above 150–200 ppm, where only 10% of the mercury in flue gas was found in the form of Hg^0 (Hall et al. 1991).

It is commonly acknowledged that, at combustion temperatures, the mercury evaporates completely from coal in the form of Hg^0 . It is only after the flue gas is cooled down to a temperature below 600°C that elemental mercury vapours react with other flue gas components, consequently leading to the formation of oxidized forms (Hg^{2+}) and Hg_p forms bound with fly ash (Fujiwara et al. 2002, Pavlish et al. 2003, Zhuang et al. 2004). The mechanism of the mercury oxidation in the presence of chlorine has not yet been unambiguously determined, but numerous studies show both homo- and heterogeneous mechanisms of the reaction between mercury and other flue gas components (Niksa et al. 2001, Lee et al. 2006, Zhao et al. 2006). The scheme of individual reactions depends on the coal characteristics (mineral and chemical composition), flue gas composition, process conditions, as well as the rate of flue gas cooling (Frandsen et al. 1994, Ariya et al. 2002, Li et al. 2003, Senior and Johnson 2005, Wichliński et al. 2014). For example, Jang and co-workers (Jang et al. 2014) proved the impact of limestone injection on the kinetics of mercury oxidation. They indicated that the gaseous oxidized mercury was more reactive with the limestone injected in the conditions of oxy-fuel combustion and the formation of particulate mercury from the oxy-fuel combustion was more efficient than from the air combustion.

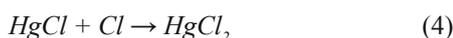
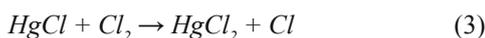
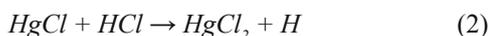
Most studies indicate a strong correlation between the chlorine content in coal and the concentrations of Hg^{2+} and Hg^0 in flue gas. It has been found that an increase in the chlorine content in fuel is accompanied by a decrease in Hg^0 in the total volume of mercury emitted from the combustion process (Hall et al. 1991, Niksa et al. 2001, Pavlish et al. 2003, Senior and Johnson 2005, Cauch et al. 2008, Jang et al. 2014). While studying transformations of Hg in the process of combustion of different coal ranks, Senior and Johnson (Senior and Johnson 2005) concluded that, in the case of lignite and subbituminous coals, the higher chlorine content in fuel brought a proportional decline in the Hg^0 concentration in the flue gas, with a simultaneous increase of oxidized Hg concentration. However, there were no such proportional relations between the concentrations of examined Hg forms for bituminous coals. Fujiwara et al. confirmed the aforementioned conclusions and described a complex mechanism of homogeneous and heterogeneous mercury oxidation (Fujiwara et al. 2002). The meaning of chlorine in reactions with mercury in combustion processes can be explained by accurate determination of the functions of all chlorine forms, i.e. atomic chlorine Cl, molecular chlorine Cl_2 , as well as HCl, both in terms of physical and chemical speciation. There is a significant impact of temperature and composition of flue gas on the kinetics and the mechanism of the Hg oxidation reaction (Rizeq et al. 1994, Widmer et al. 1998, Galbreath and Zygarlicke 2000, Ariya et al. 2002, Pavlish et al. 2003, Lee et al. 2006, Cauch et al. 2008, Jang et al. 2014, Ticknor et al. 2014). In a majority of cases, it is assumed that in the processes of thermal decomposition at the combustion temperature the chlorine in coal is released in a form of strongly reactive atomic chlorine (Horne et al. 1968, Frandsen et al. 1994, Widmer et al. 1998, Procaccini et al. 2000,

Ariya et al. 2002, Li et al. 2003, Xu et al. 2003, Wichliński et al. 2014, Jang et al. 2014). Cooling of the flue gas causes reactions which result in the formation of Cl₂ and HCl. The kinetics of these reactions depends on the rate of suppression of excited states and the stoichiometry (Senior et al. 2000, Xu et al. 2003, Agarwal and Stenger 2007, Cauch et al. 2008). Despite the very short lifetime of a chlorine atom, kinetic data show that the reaction between Cl and Hg atoms represents the dominating homogeneous reaction of oxidation, kinetically restricted by the presence of other flue gas components, mainly CO, H₂O, NO, and SO₂ (Laudal et al. 2000, Senior et al. 2000, Niksa et al. 2002, Zhuang et al. 2007a, Zhuang et al. 2007b).

Homogeneous reactions

In the combustion of coals with low chlorine content under non-equilibrium conditions, Hg⁰ may become oxidized to HgCl₂ and HgO. Senior and co-authors (Senior et al. 2000) showed that formation of HgO is crucial for coals of low chlorine content. It is estimated that in the low temperature of flue gas (<400°C), about 10% of mercury may take the form of an oxide, i.e. HgO (Rizeq et al. 1994). Relying on theoretical studies based on quantum chemistry (MP2 programme, SDD method), Xu and co-authors (Xu et al. 2003) proposed the kinetics of potential reactions leading to formation and decomposition of HgO (Table 3). They found that with the O₂ concentration of 10% v/v, from 1.5% to 6.0% of total Hg was oxidized to HgO.

The presence of chlorine in the combustion process has some influence on the kinetics and the mechanism of homogeneous reactions. Kinetic data of the elemental mercury oxidation indicate that the direct reaction between Hg and Cl₂ (at the Cl concentration of 10 ppm) in a flow reactor within the range of temperatures from 200°C to 700°C and absence of other compounds in gases is characterized by a constant rate of 1.07 x 10⁻¹⁵ cm³/mol s (Hall et al. 1991). However, due to the high activation energy of 98.29 kcal/mol (US EPA Grant No. R828168, 2004), a direct reaction between Hg and HCl, leading to the formation of HgCl, is impossible (Fuente-Cuesta et al. 2012). The mechanisms of HgCl₂ formation via homogeneous reactions of Hg⁰ and atomic chlorine are suggested to proceed according to the following equations (Niksa et al. 2001, Li et al. 2003, Zhuang et al. 2004, Zhao et al. 2006):



According to kinetic conditions, atomic chlorine may occur at flame temperature, particularly at high Cl₂ concentration. It is only after cooling down of the gas that the chlorine atoms react with HCl to form Cl₂ and hydrogen. Reaction (1) is characterized by low activation energy and may take place in room temperature at a constant rate of 1.95 ± 1.05 x 10¹³ cm³/mol s (Horne et al. 1968); the reaction has hampering influence on the mercury oxidation (Ariya et al. 2002, Li et al. 2003, Pavlish et al. 2003, Zhao et al. 2006). Sliger and co-workers (Sliger et al. 2000) proved that reaction (2) proceeds very slowly within the range of temperatures from 620°C to 1700°C, therefore, its contribution to oxidation of mercury is negligible. Reaction (3) becomes hindered under conditions of increased temperatures (>600°C). Reaction (4), on the other hand, is exothermic and only takes place next to the boundary of the energy barrier of active collisions. The foregoing considerations indicate that only two reactions with chlorine are responsible for the oxidation of Hg, and that atomic chlorine takes part in both of them. However, it should be noted that reactions (1) and (4) take place only in the area where (i) superequilibrium concentrations of Cl is observed (for temperature T>400°C) and where (ii) HgCl₂ represents the prevalent equilibrium product (T<700°C). This process model is recommended in mercury oxidation at a temperature above 800°C. Other homogeneous reactions with O₂, NO₂, and NO, and occurring at a temperature above 800°C, are limited in their extent due to kinetic constraints (Hall et al. 1991). When the flue gas temperatures are below 800°C, other flue gas components, such as HCl, Cl₂, SO₂, H₂O, and NO, take indirect or direct part in oxidation reactions (Hall et al. 1991, Widmer et al. 1998, Senior et al. 2000, Sliger et al. 2000, Xu et al. 2003, Zhuang et al. 2007, Cauch et al. 2008). Jang and co-authors (Jang et al. 2014) reported that in combustion, SO₂ reacts with oxidized mercury (HgCl₂), generating finally particulate mercury in a form of HgSO_{4(s)}. Fuente-Cuesta et al. (2012) suggested that O₂ has a synergistic effect on mercury oxidation, not only affecting it directly, but also via NO₂.

At lower temperatures (<450°C), mercury oxidation is determined by the following reaction (Niksa et al. 2001, Fujiwara et al. 2002, Zhao et al. 2006):



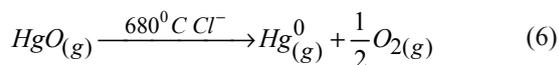
Hall et al. (1991) have suggested that reaction (5) is characterized by a constant rate of k = 3.4 x 10⁹ cm³/mol s for gases containing only mercury and 10 ppm of Cl₂. However this rate depends also on other flue gas components, i.e. CO₂, H₂O and O₂.

The impact of HCl on the mercury oxidation reaction has been extensively discussed in many papers (Hall et al. 1991,

Table 3. Kinetic parameters for mercury oxidation (adopted from Xu et al. 2003)

No	Reaction	Reaction rate constant, cm ³ /(mol s)	Activation energy, kcal/mol
1	Hg + ClO → HgO + Cl	1.38 × 10 ¹²	8.32
2	Hg + ClO ₂ → HgO + ClO	1.87 × 10 ⁷	51.27
3	Hg + N ₂ O → HgO + N ₂	5.08 × 10 ¹⁰	59.81
4	HgO + HCl → HgCl + OH	9.63 × 10 ⁴	8.92
5	HgO + HOCl → HgCl + HO ₂	4.11 × 10 ¹³	60.47

Widmer et al. 1998, Laudal et al. 2000, Senior et al. 2000, Sliger et al. 2000, Li et al. 2003). HCl is formed in high-temperature combustion zones as a result of transformation of the chlorine which is derived from coal. According to Deacon's mechanism, HCl in cooled flue gas is partially oxidized to Cl_2 in the presence of O_2 and H_2O (Ticknor et al. 2014). Oxidation of Hg by reaction with HCl takes place in flue gas within the range of temperatures from 500°C to 900°C (Senior et al. 2000). Hall et al. (1991) and Sliger et al. (2000) demonstrated that the degree of mercury oxidation increases with the increase of the HCl concentration in gases. However, Widmer et al. (1998) did not find any direct correlation between the HCl concentration and the degree of Hg oxidation, particularly at lower gas temperatures. The major difference between both studies was the composition of gases. Hall (Hall et al. 1991) and Sliger (Sliger et al. 2000) examined gases of composition similar to flue gas, whereas Widmer (Widmer et al. 1998) used a synthetic mixture with oxygen, HCl, Hg and nitrogen. These results suggested that the kinetics of HgCl_2 formation was influenced by concentrations of chlorine and HCl in flue gases. The reaction including HCl is one of those potential reactions which can lead to the formation of HgCl_2 , provided the product of the primary reaction, namely HgCl , is present in the flue gas (Equation 1). In that way, the differences between cited results can be explained. Lack of the primary reaction product (HgCl) makes the reactions between Hg and HCl leading to formation of HgCl_2 impossible. The reactions occurring in flue gas at temperatures below 600°C , in which also other flue gas components take part, result in the formation of $\text{HgCl}_{2(g)}$ and $\text{HgO}_{(g)}$. Not all the elemental mercury in flue gas is subject to oxidation, and some part of Hg^0 remains in an unchanged form. Both $\text{Hg}^0_{(g)}$ and partially $\text{HgO}_{(g)}$ occur in gases characterized by higher temperatures, however, $\text{HgO}_{(g)}$ is stable at temperatures below 400°C , whereas $\text{Hg}^0_{(g)}$ is stable above 750°C . At a temperature exceeding 600°C , in the presence of chloride, $\text{HgO}_{(g)}$ decomposition may take place according to the following reaction:



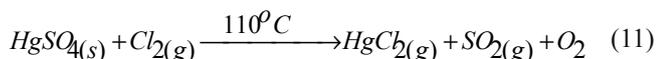
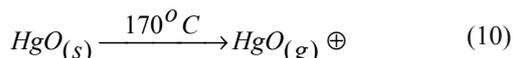
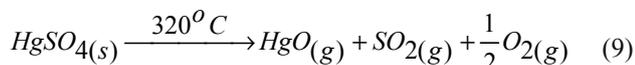
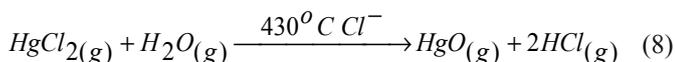
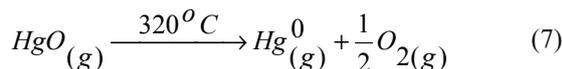
Hall et al. (1991) found out that, within the range of temperatures from 500° to 700°C , nitrogen oxides take part in reactions of oxidation of the elemental mercury, however, the rate of these reactions is lower compared to the rate of reaction of Hg^0 with Cl_2 and HCl. Therefore, it is believed that these compounds have minor impact on homogeneous oxidation of Hg^0 . Higher NO_2 concentration (ca. 1,000 ppm) causes oxidation of ca. 10% of Hg^0 at 340°C . Sliger et al. (2000) have showed that the presence of other components in flue gas, namely CO_2 , H_2O , and O_2 , reduces the efficiency of the mercury oxidation process. SO_2 does not directly react with Hg^0 in flue gas, but the presence of this compound in flue gas reduces the amount of elemental mercury being oxidized as a consequence of the reaction with HCl (Ghorishi 1998, Edwards et al. 2001, Naruse et al. 2010). Similar dependences were observed while studying the impact of steam on mercury oxidation (Ghorishi 1998). However, the presence of CO in flue gas contributes to formation of Cl and HgCl_2 (Edwards et al. 2001).

In the course of a laboratory-scale study on the influence of concentration of Cl, SO_2 , HCl, and fly ash on speciation of Hg in gases of compositions similar to the flue gas emitted in the coal combustion process, Laudal et al. (2000) found that the presence of chlorine in the gas caused an increase in the ionized mercury forms in total mercury content in gas to the level of ca. 85%. On the other hand, reduction of Hg^{+2} concentration to the level of 1% was also observed when fly ash was present. The same relation was observed in cases of SO_2 being present in gases. Laudal and co-authors (Laudal et al. 2000) did not determine any influence of HCl concentration on the efficiency of the Hg oxidation reaction. Studies on Hg transformations in gases in a form of mixtures of fly ash, Cl_2 , and SO_2 revealed that the Hg^{2+} represented 25.5% of the total mercury content. This fraction was lower when compared to the results obtained while testing gases containing Cl_2 only, but higher than those obtained in studies where the gas contained fly ash or SO_2 . All these results suggest that the presence of SO_2 and fly ash in gases hamper and/or slow down reactions of mercury oxidation. Similar behaviour of mercury was observed while testing gases with SO_2 , HCl, and Cl_2 (Laudal et al. 2000).

Other components present in flue gas are nitric oxides (NO and NO_2). In the gases containing mercury vapours and nitric oxides only, the oxidized forms of mercury constituted about 2.5% of total Hg concentration, whereas the addition of fly ash and chlorine to the gas caused an increase in Hg^{+2} content to 78.5%. Such considerable content of Hg^{+2} in gases highlights the major role of chlorine in the mercury oxidation reactions. However, it is noted that the results obtained by Laudal et al. (2000) were based on examinations of synthetic gas conducted at a temperature not corresponding to the actual flue gas temperature. Bearing in mind the impact of the flue gas temperature on the kinetics of the oxidation reaction, it is impossible to make a direct reference between the results thus obtained and the conditions of combustion (Niksa et al. 2001) make the reactions with HCl leading to formation of HgCl_2 impossible.

Impact of temperature and carbon content on Hg speciation

Numerous studies have also been conducted on establishing the impact of flue gas temperature on the speciation of mercury emitted in coal combustion processes (Hall et al. 1991, Frandsen et al. 1994, Dajnak et al. 2003, Tan et al. 2004, Wang et al. 2010). In the process within the range of temperatures from 250°C to 400°C with lignite and subbituminous coals characterized by high chlorine content, mercury is mainly removed as Hg^0 (Tan et al. 2004), whereas in the flue gas emitted in combustion of the bituminous coal, and cooled to the temperature of 200°C , 80% of the total mercury present in the gaseous phase is in its oxidized forms (Tan et al. 2004, Wang et al. 2010). Because of lower temperature of flue gas and higher chlorine concentration, ca. 75% of Hg becomes bound with particulate matter, forming Hg_p . The presence of chlorine in flue gas determines the mercury oxidation reactions as well as the physical speciation of Hg. The presence of chlorine results in decrease in the temperature of mercury transformation from the solid to the gaseous phase. Frandsen et al. (1994) have proposed a model of conversion of mercury compounds in flue gas at temperatures below 450°C .



\oplus – excluding $\text{HgSO}_{4(g)}$ presence, (s) – solid phase, (g) gaseous phase

The presence of $\text{HgSO}_{4(s)}$ and $\text{HgO}_{(s)}$ is thermodynamically justified within flue gas temperatures from 110°C to 320°C (Frandsen et al. 1994). Based on equilibrium calculations for temperatures below 125°C, Dajnak et al. (2003) concluded that $\text{HgSO}_{4(s)}$ is the main form of mercury condensed from flue gas components. They also found that mercury condenses as HgCl_2 at temperatures between 125°C and 520°C, and it occurs mainly in elemental form at temperatures above 520°C.

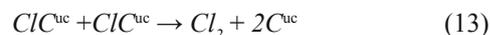
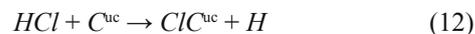
Senior et al. (2000) observed that mercury transformations also depend on the flue gas cooling rate. Higher efficiency of Hg oxidation was observed when the gas cooling rate was lower. For the gas cooling rate of 73°C/s, the Hg conversion factor came to 24%, whereas at a cooling rate of 250°C/s – 10.5% of Hg became oxidized in a comparable period of time. Hall et al. (1991) proved that the mercury oxidation rate depends on temperature of gases. An increase in the gas temperature results in increase of the oxidation rate. Such a relation has been observed up to the gas temperature of 900°C.

Heterogeneous reactions

It is claimed that mercury can be oxidized in flue gas by catalytic heterogeneous reactions leading to the formation of Hg^{2+} (Liu et al. 2001, Meij et al. 2002, Pavlish et al. 2003, Laumb et al. 2004, Park et al. 2008, Bhardwaj et al. 2009, Gao et al. 2013). These reactions are initiated in flue gas which is cooled to a temperature below 600°C. Numerous publications indicate a strong relation between the chlorine content in coal, the concentration of Hg^{+2} in flue gas, and the amount of Hg bound with the solid phase (Liu et al. 2001, Meij et al. 2002, Pavlish et al. 2003, Park et al. 2008). Higher chlorine content in coal leads to increased efficiency of Hg oxidation, and also to a higher content of fly ash-bound mercury. Results from the studies focused on mercury conversion in flue gas discussed by Fujiwara et al. (2002) have proved that only combustion of coals with considerable chlorine content leads to the formation of large amounts of mercury in its oxidized form, however, the observed Hg oxidation efficiency did not rise with the increase of the time of Hg remaining in flue gas. In the case

of flue gas cooling, distribution of mercury between solid and the gaseous phase changes towards an increase in the content of solid particle-bound Hg. Efficiency of heterogeneous reactions of mercury oxidation depends on a number of factors, including flue gas temperature and its composition, mainly on the concentration of NO_2 , HCl, NO and SO_2 (Hall et al. 1991, Galbreath and Zygarlicke 1996, Galbreath and Zygarlicke 2000, Dajnak et al. 2003) as well as on the specific surface area of grains and the content of minerals and unburned carbon in fly ash (Pavlish et al. 2003).

The results of studies undertaken by Galbreath and co-workers (Galbreath et al. 2004) indicate that the addition of 100 ppm of HCl to the flue gas increased the efficiency of the mercury oxidation reactions as well as mercury adsorption on fly ash surfaces. Heterogeneous reactions with chlorine and mercury may be divided into two groups: (i) direct binding of mercury on the surface and (ii) indirect Hg oxidation as a consequence of the heterogeneous reaction on the coal surface containing Cl atoms, leading to the formation of Cl_2 (Gao et al. 2013). The heterogeneous submechanism of oxidation assumes that chlorine atoms are substituted with mercury atoms on the surface of coal. Results of some studies (Hower et al. 2000, Sakulpitakphon et al. 2000, Mardon and Hower 2004, Mastalerz et al. 2004, Lopez-Anton et al. 2007, Suárez-Ruiz and Parra 2007, Suárez-Ruiz et al. 2007, Hower et al. 2010) suggest that the unburned carbon (C^{uc}) facilitates the conversion of HCl in flue gas into chlorine derivatives of carbon which may react with elemental mercury according to the following reaction patterns (Lopez-Anton et al. 2009):



An XPS analysis revealed that chlorine on coal surfaces occurs in a form of chlorides as well as in organic forms (Laumb et al. 2004).

The efficiency of heterogeneous reactions taking place on the surface of fly ash also depends on the flue gas composition, and particularly on the concentration of NO_2 , HCl, NO, and SO_2 (Norton et al. 2003, Hower et al. 2010, Fuente-Cuesta et al. 2012). The study undertaken by Norton et al. (2003) into the influence of flue gas components on mercury oxidation in gases with vapours of Hg, NO, NO_2 , CO, CO_2 , O_2 , and H_2O , transferred through fly ash filters of different carbon content and different specific surface area at the temperature of 180°C, has shown that NO_2 , HCl, and SO_2 facilitate mercury oxidation in heterogeneous reactions, whereas the oxidation reaction efficiency decreases in the presence of NO. Moreover, a decline in the oxidation efficiency was observed (only 1% of elemental mercury was subject to oxidation) when there was no ash in the gas, whereas in the presence of fly ash of carbon content of 3.6% and specific surface area of 3.4 m^2/g , 14% of mercury was oxidized. Utilization of a fly ash filter with low carbon content of 0.08% and low specific surface area of 1.5 m^2/g resulted in oxidation of 4% of elemental mercury in the gas. The results clearly show that by increasing the carbon content in the fly ash and by expanding its specific surface area, it is possible to raise the efficiency of the mercury oxidation reaction in flue gases.

Results from the studies aimed to evaluate the influence of gas temperatures on the efficiency of the oxidation reaction showed that a drop in the gas temperature to 120°C caused an increase in the mercury oxidation efficiency up to a level of 10% for fly ash with low carbon content and small specific surface area. It was also found out that lower flue gas temperatures facilitated mercury adsorption on the solid particulates, while oxidation of adsorbed Hg took place at temperatures below 150°C (Norton et al. 2003).

Together with heterogeneous mercury oxidation reactions, reactions with HCl, oxygen, or NO₂ may also take place, leading to the development of reactive forms contributing to heterogeneous mercury oxidation. Dunham et al. (2003) and Olson et al. (2005) proposed a detailed mechanism of heterogeneous Hg oxidation reactions occurring in the presence of NO₂ and SO₂. In the presence of NO₂, elemental mercury is catalytically oxidized into coal surface-bound Hg(NO₃)₂, whereas in the presence of SO₂, mercury is converted into its sulphate form. The sulphur compounds in flue gas together with HCl displace chlorine from the coal surface, thus increasing the content of oxidized forms of mercury in flue gas. What still requires explanation is the thermodynamic and kinetic constraints in mercury and chlorine interrelations in flue gas.

Heterogeneous reactions are catalysed by certain ash components. Iron oxides and/or calcium and copper compounds in the ash can catalyse these types of reactions (Ghorishi and Gullett 1998, Niksa and Fujiwara 2005, Senior 2006, Zhuang et al. 2007, Abad-Valle et al. 2011). The catalytic effect of CuO and Fe₂O₃ is increased as a consequence of the presence of HCl and NO_x in the flue gas (Bhardwaj et al. 2009). Diversified influence of iron compounds on the catalytic reactions taking place in flue gas has also been observed and, therefore, the addition of hematite contributes to mercury oxidation while the addition of hematite and NO₂ inhibits reactions of this type (Galbreath et al. 2004). Dunham et al. (2003), on the other hand, found a correlation between the content of magnetite in ash and Hg oxidation, and the results of their studies indicate that efficiency of the Hg oxidation reaction increases with the increase of the magnetite content in the ash. Based on that, a suggestion has been made that iron oxide in spinel-type structures in fly ash facilitates mercury oxidation. No catalytic effect has been observed in the cases of SiO₂, Al₂O₃, and Ca(OH)₂ (Ghorishi and Gullett 1998), whereas Lee et al. (2000) have determined that in the presence of NO_x both SiO₂ and Al₂O₃ display catalytic properties for the reactions of Hg oxidation. Other inorganic ash components with catalytic properties towards airborne mercury do not display them in the case of flue gas.

The iron which is present in fuels catalyses oxidation and binds mercury. In the combustion process, on the other hand, calcium reacts with chlorine, thus leading to the formation of CaCl₂, and this reaction is competitive with the reaction of Hg oxidation by chlorine. While studying transformations of subbituminous coal with CaCl₂ additives, Zhaung et al. (2007) arrived at a conclusion that addition of this compound resulted in oxidation of ca. 50% of the elemental mercury in flue gas. These reactions are responsible for high Hg⁰ content in the total emission of mercury from combustion of lignite and subbituminous coals characterized by high calcium content and low chlorine content. In the study on thermal stabilisation of mercury retained on the fly ash, Rubel et al. (2005)

demonstrated thermal stability of mercury in ash samples up to 300°C. Results of their studies suggest a correlation between the efficiency of mercury retention on the fly ash and the increase of its sulphur and carbon content. It has also been determined that the carbon content in fly ash is responsible for predominant form of Hg sorption, i.e. chemisorption of this element. The presence of sulphur in fly ash, on the other hand, causes Hg deposition in the form of sulphur compounds.

Mercury adsorption on the fly ash surface

As mentioned above, fly ash takes part in heterogeneous oxidation of mercury. It is also mercury adsorbent, but the adsorption capacity of inorganic fly ash fractions is low for mercury. The numerous attempts made to determine the relation between carbon or volatile matter content and the efficiency of gaseous mercury sorption on the ash, in most cases have indicated considerable influence of the specific surface area, the content of mineral particulate fractions in the ash, and the flue gas temperature (Baochun et al. 2000, Gibb et al. 2000, Fujiwara et al. 2002, Dunham et al. 2003, Tan et al. 2004, Maroto-Valer et al. 2005, Rubel et al. 2005, Rubel et al. 2006, Wang et al. 2007, Hower et al. 2010, Abad-Valle et al. 2011). Mercury in the form of HgO and Hg²⁺ may be subject to partial sorption on the fly ash which contains considerable quantities of unburned carbon, and such phenomenon was observed in hot flue gas, above the temperature of 500°C (Baochun et al. 2000, Fujiwara et al. 2002, Wang et al. 2007, Abad-Valle et al. 2011). In the measurements conducted during coal combustion in a 1 MW furnace, Gibb et al. (2000) found out a relation between the carbon content in the ash and the efficiency of sorption on its surface. Results of their studies suggest that nearly 100% of mercury emitted from coal combustion was retained on the surface of the ash which contained more than 5% of unburned carbon. They demonstrated a linear correlation between a decline in the flue gas temperature and an increase in the Hg content in fly ash within the range of flue gas temperatures from 150°C to 450°C (Gibb et al. 2000, Rubel et al. 2005). Additionally, they found out that the efficiency of Hg sorption on fly ash increased with the time of effective contact between flue gas and fly ash (Rubel et al. 2006). Tan et al. (2004), in a study on mercury speciation in the flue gas emitted in coal combustion in a vertical combustion chamber, found that 12% of the total emitted mercury was subject to sorption on the surface of high-carbon ash.

No relation between the chlorine content in coal and the efficiency of mercury retention on the particulate was observed (Hower et al. 2010), however the results of studies by Dunham et al. (2003) show that sorption capacity of the ash emitted in the coal combustion process is very similar to HgCl₂ and Hg⁰, and that it increases with the temperature decrease. Other relations were established by Baochun et al. (2000) while testing adsorption of gaseous mercury on the ash within the temperature range from 70°C to 160°C. They suggest that, under identical conditions and depending on the type of coal from which the ash has been produced, adsorption of mercury in the form of HgCl₂ is ca. 2 to 50 times more effective than Hg⁰ adsorption. Adsorption of HgCl₂ is less dependent on carbon content in the coal from which the ash was produced and depends more on the ash specific surface area (Galbreath and Zygarlicka 2000). The results thus obtained show that

sorption of HgCl_2 on the surface of ash is a physical adsorption process.

The phenomenon of mercury adsorption on the ash is also affected by the flue gas composition. Wang et al. (2007) found out that high concentration of ammonia in gas limited mercury adsorption, in the result of the formation of a mercury-ammonia complex, characterized by lower capacity for adsorption on solid particulates.

Conclusions

Mercury transformation mechanisms and speciation characteristics were reviewed for mercury compounds emitted in flue gas from coal-fired boilers. As confirmed in numerous publications, chemical conversion of mercury and its compounds into flue gas indicate that in the combustion process three main stages of different kinetics and reaction mechanisms can be distinguished. The first one is the stage of mercury evaporation from fuel, when decomposition of mercury compounds takes place together with reactions leading to the formation of elemental mercury (Hg^0). This stage takes place at temperatures exceeding 700°C . The second stage comprises homogeneous reactions of Hg^0 oxidation with other active flue gas components, predominantly HCl , which leads to the formation of HgCl_2 and HgO . These reactions take place mainly at a temperature below 600°C , and their kinetics depends on the concentration of flue gas components. Heterogeneous reactions with participation of mercury, both in the elemental and the oxidized form, and leading to the generation of particulate-bound forms of Hg , take place at temperatures below 600°C . However, the particulate-bound form is stable up to a flue gas temperature of about 300°C . Both homo- and heterogeneous reactions depend on the concentration of gaseous components of flue gas, while the heterogeneous ones depend also on fly ash properties, such as the content of elemental carbon and mineral fraction as well as the specific surface area of ash particles.

Awareness of the issue of mercury as a global pollutant is growing and, as a result, emission reduction requirements are becoming more common. Thus, the explanation of the mechanisms of mercury release in coal combustion units is a fundamental part of an emission-control strategy. Although there are a number of different technical approaches to remove mercury from flue gas, there is no single best technology that can be implemented broadly. Most of the discussed here issues concerning transformation of mercury and its compounds in coal combustion have a substantial connection with decisions on selection of a method of mercury emission reduction to the atmosphere. Having in mind this knowledge one can decide if a better choice is a particulate emission control technique, an adsorption or absorption method as a mercury emission control technology.

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Przemiany rtęci w procesach spalania paliw stałych

Streszczenie: Artykuł stanowi podsumowanie aktualnego stanu wiedzy nt. kinetyki i mechanizmów reakcji z udziałem rtęci, w tym reakcji homogenicznych i heterogenicznych, zachodzących w spalinach z procesów spalania paliw stałych. Opisano wpływ składników spalin i temperatury na efektywność utleniania rtęci. Omówiono również zagadnienia fizycznej i chemicznej specjacji rtęci w gazach spalinowych, jak również wpływ różnych czynników na specjację rtęci.