

Mitigation of gaseous mercury emissions from waste-to-energy facilities: homogeneous and heterogeneous Hg-oxidation pathways in presence of fly ashes

Rumayor M.^{a,b*}, Svoboda K.^{a,c}, Švehla J.^a, Pohořelý M.^a, Šyc M.^a

^a Institute of Chemical Process Fundamentals of the CAS, v. v. i., Rozvojová 135, 165 02
Praha 6, Czech Republic

^b University of Cantabria, Department of Chemical and Biomolecular Engineering, Av.
Los Castros s/n, Santander, Spain

^c Faculty of the Environment, University of Jan Evangelista Purkyně, Králova Výšina 7,
400 96 Ústí nad Labem, Czech Republic

*** Corresponding author:** Marta Rumayor

University of Cantabria, Department of Chemical and Biomolecular Engineering

Av. Los Castros s/n, 39005 Santander, Spain

E-mail: marta.rumayor@unican.es; rumayor@icpf.cas.cz

Tlf: (+34) 942 20 67 49

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

Abstract

This study describes the main mechanisms that take part in the mercury homogeneous oxidation pathway in presence of some of the main reactive compounds formed during waste incineration processes (O_2 , HCl, SO_2 and NO). Series of model, synthetic dry flue gases were used to elucidate the effects of HCl, SO_2 , NO and their proportions in the gas on mercury behaviour. Three samples of fly ash collected from a I facility were characterized and evaluated both for Hg heterogeneous oxidation and Hg removal in a laboratory scale device. The results obtained in this study showed that homogeneous mercury oxidation in the models MSWI and coal combustion flue gas atmospheres was $52 \pm 5\%$ and 25% , respectively. SO_2 , NO and HCl have a synergetic effect in Hg oxidation in presence of oxygen, but the main differences found are mainly caused by the strong influence of HCl and the likely inhibitory oxidation effects of SO_2 . Surface area together with carbon and chloride content of the fly ashes were correlated with their capacity for Hg- heterogeneous oxidation and adsorption. The sample of fly ash with relatively high content of unburnt carbon and chlorine, and with BET surface ($2.42 \text{ m}^2/\text{g}$) was able to remove up to 100% of $Hg^0(g)$ during 300 min. The results obtained in this study provide a complete overview of the behaviour of mercury during MSWI processes and may help to clarify the fate/behaviour of mercury in a filter (e.g. electrostatic precipitator) providing a deeper knowledge about the impacts of fly ash properties on mercury fate in waste incineration.

Keywords: mercury, waste to energy, oxidation, fly-ash, capture

1. Introduction

Waste-to-energy (WtE) plants are an attractive solution all over the world for managing the huge production of Municipal Solid Waste (MSW). Incineration process reduces the volume of waste and provides energy which is recovered from the combustion of MSW. Nevertheless, it is not a simple solution because the incineration generates some dust and gaseous pollutants that must be removed by means of air pollution control devices (APCD). The solid, slurry or liquid waste from flue gas cleaning processes must subsequently be properly disposed of with minimization of their environmental impacts. The common pollutants generated in Municipal Solid Waste Incineration (MSWI) are SO_2 , HCl , NO_x , dust and more volatile heavy metals, including mercury (Hg) (Waldner *et al.*, 2013). The Minamata Convention classified waste incineration facilities as point sources of emissions of Hg^0 and Hg^{2+} compounds to the atmosphere, together with coal-fired power plants, non-ferrous metals and cement clinker production processes (UNEP, 2013). The sources of mercury in MSW include mainly batteries, paint residues, thermometers, thermostats, light switches, luminescent tubes, etc. (Riber *et al.*, 2009; Cheng and Hu, 2012). Despite the fact that current trends show a decrease of mercury-containing products in waste, and hence also decreasing Hg emissions from MSW incineration (MSWI), exceptionally, the content of mercury in MSWI flue gas can achieve significant values which should be safely reduced below the prescribed limits (Van Veizen and Langenkamp, 2002).

When elemental mercury (Hg^0) is released from the incineration hot zone (850-1200 °C) into the flue gas, it undergoes gradually a large number of homogeneous and heterogeneous oxidation processes in boiler and in the air pollution control devices (APCDs). Elemental mercury (Hg^0) in vapour state is the most difficult Hg-species to control because of its insolubility in water and high volatility. Hg^0 emissions are generally

an issue of special concern (Pavlish *et al.*, 2003). Nevertheless, Hg^0 is partly oxidized in flue gas and some of such Hg species ($\text{Hg}^{2+}(\text{g})$) formed in the flue gas may react with the solid particles being partially captured and removed in the gas cleaning lines, which means a reduction of mercury emissions from the stack. Mercury captured by fly ash particles (Hg_p) is easily removed by dust removal control devices such as electrostatic precipitators (ESP), bag filters, etc. Oxidized form of mercury ($\text{Hg}^{2+}(\text{g})$ species), such as HgCl_2 , are water soluble and can be easily removed by existing wet type APCDs, like wet (hot water) removal of HCl, wet flue-gas desulfurization (WFGD). The overall removal efficiency of mercury from flue gas is connected with the partitioning of mercury species: the higher the ratio of oxidized to elemental mercury, the higher the mercury removal efficiency (Pavlish *et al.*, 2003). Waste-to-energy facilities use also a dry/semidry scrubbing system for removing acidic gases in combination with a fabric bag filter for capturing fly ash particles and sorbent (e.g. activated carbon) injection for removal of various organic micro-pollutants (e.g. dioxins/furans (PCDD/PCDF), PAH and PCB. The combination of these APCDs displays an efficiency of Hg removal over 60% (Zhang *et al.*, 2008). Flue gas cleaning processes generate some solid residues loaded with mercury, such as fly ash or FGD-gypsum that are usually classified as hazardous wastes. These solid/slurry residues from gas cleaning processes must be deposited or stabilized/solidified, taking always into account the final form of Hg coming into contact with the environment.

The ability to determine both the Hg speciation and its interactions during the residence time in the gas cleaning process is the key factor to improve and develop better Hg-control strategies and manage the Hg-loaded solid residues generated in the gas cleaning process. Flue gas composition and gas cleaning process conditions (e.g. temperature and kinds of air pollution control devices (APCDs)) modify the Hg interactions, its speciation

and its final distribution. Data on behaviour and distribution of mercury can be found in literature, both for WtE plants (Svoboda *et al.*, 2016, Hall *et al.*, 1990, Gasper *et al.*, 1997; Widmer *et al.*, 1998, 2000) and coal combustion processes (Naruse *et al.*, 2010, Xu *et al.*, 2003, Niksa *et al.*, 2001). Heterogeneous oxidation of mercury on the surface of fly ash particles is as important (or even more important in the case of coal combustion) as the homogeneous oxidation of mercury (Niksa *et al.*, 2010). Some mercury interaction/retention mechanisms have already been proposed in fly ashes from coal-fired power plants (López-Antón *et al.*, 2009; Zhao *et al.*, 2010; Xu *et al.*, 2013; He *et al.* 2016; Yang *et al.*, 2016), but there is still a lack of available studies concerned about fly ashes from MSWI. On the basis of knowledge acquired so far, this study aims to assess the gaseous behaviour of mercury and the interactions between mercury species and fly ashes collected in a WtE incineration facility. For this purpose, a lab scale fixed-bed experimental device was designed, built and optimized. A comparison between Hg retention capacities under MSWI and coal combustion in air atmospheres was done demonstrating the main interaction pathways and the differences between Hg-fly ash interactions in both model flue gases. This study allows:

- (i) to identify the different gaseous mercury interactions (gas-gas) that occur as a result of the main components present in MSWI gas atmosphere with respect to the most studied coal combustion gas atmosphere.
- (ii) to propose and to understand the mechanisms via which different species of mercury are retained in the fly ashes (gas-fly ash) throughout the three parts of the flue gas path (boiler and filters) of a particular Waste to Energy facility.

2. Materials and methods

2.1. Samples

Three samples of fly ash from a WtE facility were used in this study. The MSWI facility is fed by mixed municipal solid wastes (MSW), the maximum temperature in the incineration part is 1180 °C. The capacity of the MSWI facility is about 96 000 ton of waste/year and it has an approx. production of 13 GWh of electric energy and 700 TJ of useful heat energy per year. The samples, labelled as FA1, FA2 and FA3, were collected from the 2-nd and 3-rd boiler pass, the 4-th boiler pass and from the ESP of the plant, respectively (Figure 1). These samples were properly homogenised and characterized. The unburnt carbon content was estimated as loss on ignition (LOI) by combustion of the organic matter at 815 °C. The chemical composition was determined by XRF (X-ray fluorescence); sulphur oxidation state was checked by X-ray Photoelectronic Spectroscopy (XPS). The Brunauer–Emmett–Teller (BET) surface area was determined by volumetric adsorption of nitrogen at 77 K. The contents of chlorine were analysed by ion chromatography (IC) after an oxidative high-pressure digestion. The content of mercury in the original fly ash samples was determined by means of an Advanced Mercury Analyzer AMA254 (LECO).

HSC chemistry software was used to predict the theoretical speciation of Hg in gas phase in the complete atmospheres.

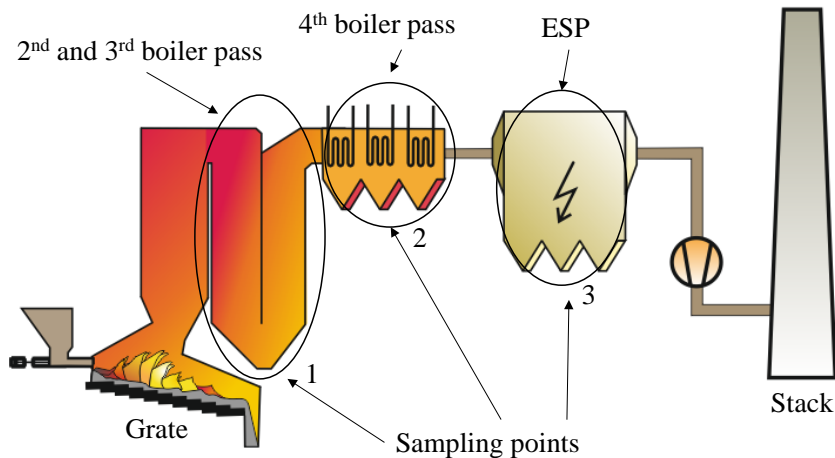


Figure 1. Scheme of the WtE facility with sampling points for the samples (FA1, FA2, FA3)

2.2. Experimental device for mercury capture

A lab-scale device was specifically designed and built to carry out the Hg oxidation and capture experiments. All the pipes used were composed of polytetrafluoroethylene (diameter 6 mm) to prevent possible mercury attacks/sorption and memory effects. Those pipes where gaseous mercury is present were heated by controlled heating tapes and kept at temperatures of 120-140 °C to avoid condensation of Hg⁰/Hg²⁺ compounds. The experimental device (Figure 2) consists of: (i) a set of four Bronkhorst mass flow controllers (MFCs) and two rotameters (OMEGA) which served for simulation of gas atmospheres used in the study (Table 1) (ii) a certified VICI Metronic Hg⁰-permeation tube and a Dynacalibrator 150 unit with a thermostat (Valco Instruments Company Inc.) were used for generation of the needed constant concentration of Hg⁰ in the flue gas (at the entrance of the tube reactor) of 100 µg·m⁻³, (iii) a quartz tube reactor (diameter, 25

mm) heated by a furnace (Carbolite Gero). A fly ash bed (0.030 g of sorbent in 4 g of fine quartz sand) was used in the case of heterogeneous (gas-fly ash) studies. The bed was placed on a frit in the middle part of the quartz tube, and (iv) a system for determining the mercury species (Hg^0 and Hg^{2+}). This system consists of an on-line elemental mercury analyser VM3000 (Mercury Instruments) serving for continuous measurement of Hg^0 vapour concentration downstream the fixed-bed reactor (sorbent) and downstream the unit with the selective sorption/removal of gaseous oxidized mercury (Hg^{2+}). VM3000 is based on cold vapor atomic absorption spectroscopy (CVAAS) method where light absorption measurement takes place at a wavelength of 253.7 nm. The Hg^{2+} was captured by means of a conditioned-ion exchanger resin Dowex® 1 × 8 (The Dow Chemical Company), suitable for the selective extraction of Hg^{2+} species (Fuente-Cuesta *et al.*, 2014) at the flue gas temperature (120-140 °C). Prior to the application, the resin was conditioned with a solution of HCl:H₂O (1:1) at 90 °C during 30 min and then filtered and dried. 1.5 g of the resin was situated upstream the Hg^0 vapour analyser in a fixed bed reactor. Both the Hg^{2+} content in the resin and the total mercury content captured by the fly ash sample (Hg_p) were determined by means of an automatic mercury analyser AMA 254 (LECO Corporation) (Sysalová *et al.*, 2013). All balances were ensured to be accurately closed with a precision lower than 10%. Five pieces of thermocouples (K type) were placed in the most important/critical points of the device (one of the thermocouples was situated near the sorbent sample inside the tube) to make sure that there was no cold or overheated zone (with mercury losses or damage of the tubes, respectively). Each of the variables (five temperatures, Hg^0 signal from the VM3000 analyser and gas flow rates measured and controlled by the MFCs) were continuously registered/recorded in the computer by a LabView software (National Instruments).

The efficiency of Hg⁰ removal (η) was determined during the running time by the equation (1):

$$\eta(\%) = \left[1 - \frac{C_{out}}{C_{in}} \right] \times 100 \quad (1)$$

C_{out} and C_{in} are the Hg⁰ concentrations at the outlet and inlet ($100 \mu\text{g}\cdot\text{m}^{-3}$) of the fixed-bed reactor, respectively.

Table 1. Atmospheres used in the Hg-homogeneous and Hg-heterogeneous oxidation experiments

Atmosphere	CO ₂ (% v/v)	O ₂ (% v/v)	N ₂ (% v/v)	HCl (ppm-v)	SO ₂ (ppm-v)	NO (ppm-v)
Inert	-	-	100	-	-	-
MSWI	10	5	Balance	600	300	200
Air-CC	10	5	Balance	25	1000	1000
HCl_1-3	-	3	Balance	300/600/900	-	-
HCl_4	10	5	Balance	600	-	-
NO_1-2	-	-	Balance	-	-	200/400
NO_3	10	5	Balance	-	-	200
SO ₂ _1-3	-	-	Balance	-	200/400/800	-
SO ₂ _4	10	5	Balance	-	400	-
NO_SO ₂	10	5	Balance	-	400	200

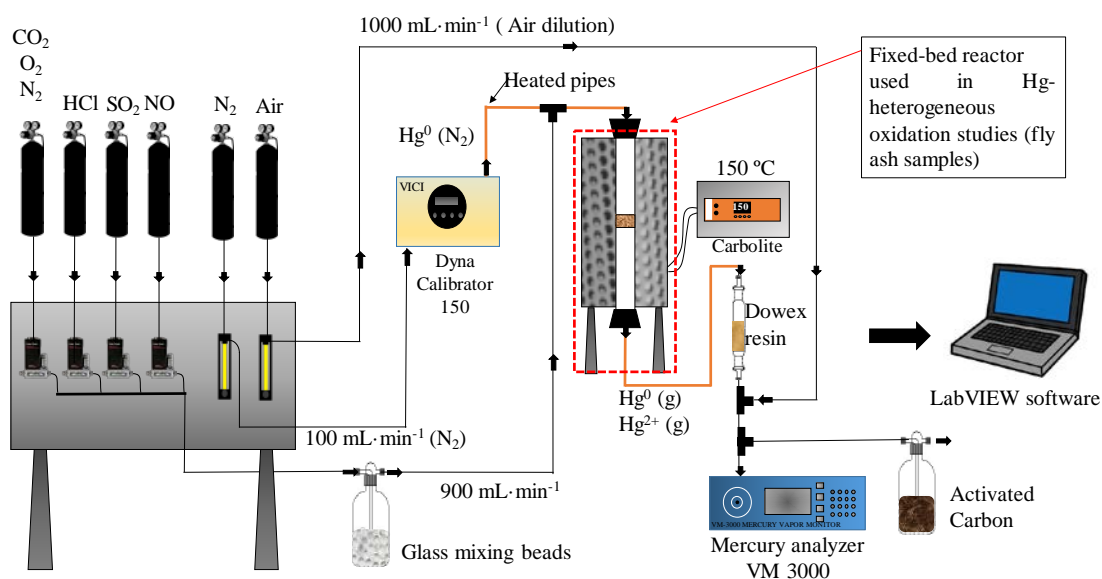


Figure 2. Schematic diagram of the experimental device for Hg-homogeneous and Hg-heterogeneous oxidation studies.

3. Results and discussion

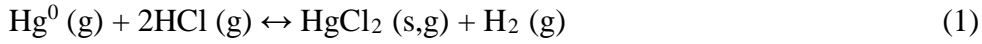
The composition characteristics for the ash samples FA1, FA2 and FA3 can be shown in the Supplementary data. The inorganic components indicate that the fly ash samples are mainly constituted of CaO, SiO₂ and Al₂O₃, among others, at different stages of transformation and they contain heavy metals (such as Hg, As) and Se. As it was expected, these trace elements are concentrated in the sample with higher BET surface and lower particle size (FA3). Unburnt carbon content, estimated by LOI, increased with increasing BET surface FA1<FA2<FA3. The results obtained by X-ray Photoelectronic Spectroscopy (XPS) indicate that all the samples (FA1, FA2, FA3) contained only sulphates (SO₄)²⁻ (more than 70 %) and sulphites (SO₃)²⁻ and there was no detectable content of sulphides (S)²⁻ in the samples.

3.1. Mercury homogeneous oxidation study

First series of experiments were carried out in order to evaluate the effects caused by the components present in typical flue gas from MSWI and air-coal combustion (Air-CC) (SO_2 , NO and HCl) in the homogeneous oxidation of Hg (gas-gas interactions). The studies were performed in the experimental device, described in the section 2.2. The inlet content of $\text{Hg}^0(\text{g})$ was $100 \mu\text{g}\cdot\text{m}^{-3}$ and the reactor tube was kept empty. Both the $\text{Hg}^0(\text{g})$ and $\text{Hg}^{2+}(\text{g})$ at the outlet were determined under fourteen flue gas composition schemes (Table 1). The temperature was kept at $150 \text{ }^\circ\text{C}$ and the gas residence time in the experimental system was approx. 9 s.

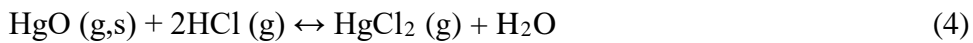
Influence of HCl and chlorine species. The gas-phase Hg oxidation extent results have shown that homogeneous oxidation of Hg depends mainly on the reaction between elemental mercury and the present halogen compounds (HCl). It is known that elemental mercury ($\text{Hg}^0(\text{g})$) could be directly oxidized by HCl , in presence of O_2 and chlorine species that would favour the reaction at low temperatures. First tests were done in an atmosphere of N_2 and O_2 (3% v/v) adding three different concentrations of HCl (HCl_1 -3). Another atmosphere containing CO_2 (10% v/v), O_2 (5% v/v) and 600 ppmv of HCl (HCl_4) balanced with N_2 was subsequently tested. Figure 3(a) shows the percentages of both $\text{Hg}^0(\text{g})$ and $\text{Hg}^{2+}(\text{g})$ obtained after 3 hours. The percentages of $\text{Hg}^0(\text{g})$ and $\text{Hg}^{2+}(\text{g})$ were determined by the continuous Hg^0 analyser VM3000 and sorption/capture of Hg^{2+} in the suitable ion exchanger resin (Dowex) respectively. It is known that for normal concentrations of HCl in MSWI flue gas, mercury chloride (HgCl_2) is the dominant Hg compound present in such a flue gas (Senior *et al.*, 2000, Svoboda *et al.*, 2016). The results obtained in this study confirm the clear influence of HCl on the Hg oxidation extent, ranging from 8% up to 34% of Hg^{2+} . The elementary reaction between Hg and HCl in inert gas (1) is hindered by a very high energy barrier (Hranisavljevic and Fontijn, 1997; Sliger *et al.*, 2000), however due to the relatively high concentration of HCl

together with oxygen in MSWI flue gas atmospheres, reaction (2) can be considered as an oxidation pathway in some detail.

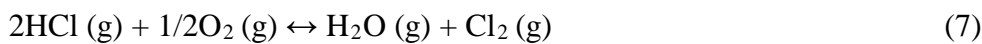
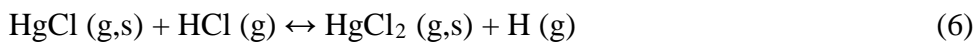


Because the atmospheres HCl_1-3 contain 3% of oxygen, the proposed homogeneous oxidation pathway in this study is based on the mechanism postulated by Hall *et al*, 1990.

Hg^0 is oxidized to HgO (3) by oxygen, which acts as an intermediate in the formation of HgCl_2 (4).



It has been also suggested that the oxidation could occur via intermediates derived from HCl, such as atomic chlorine or Cl_2 whose concentration increases under 200 °C, these intermediates allow a fast mercury oxidation rate (reactions 5-6). However, it was demonstrated that the conversion of HCl to Cl_2 in the flue gas conditions is kinetically limited (Senior *et al.*, 2000) and it needs to be catalysed by particles to trigger the Deacon process described in Eq. (7) (Deacon, 1875). This mechanism is ruled out in the conditions of this section but it could occur when fly ash particles are present.



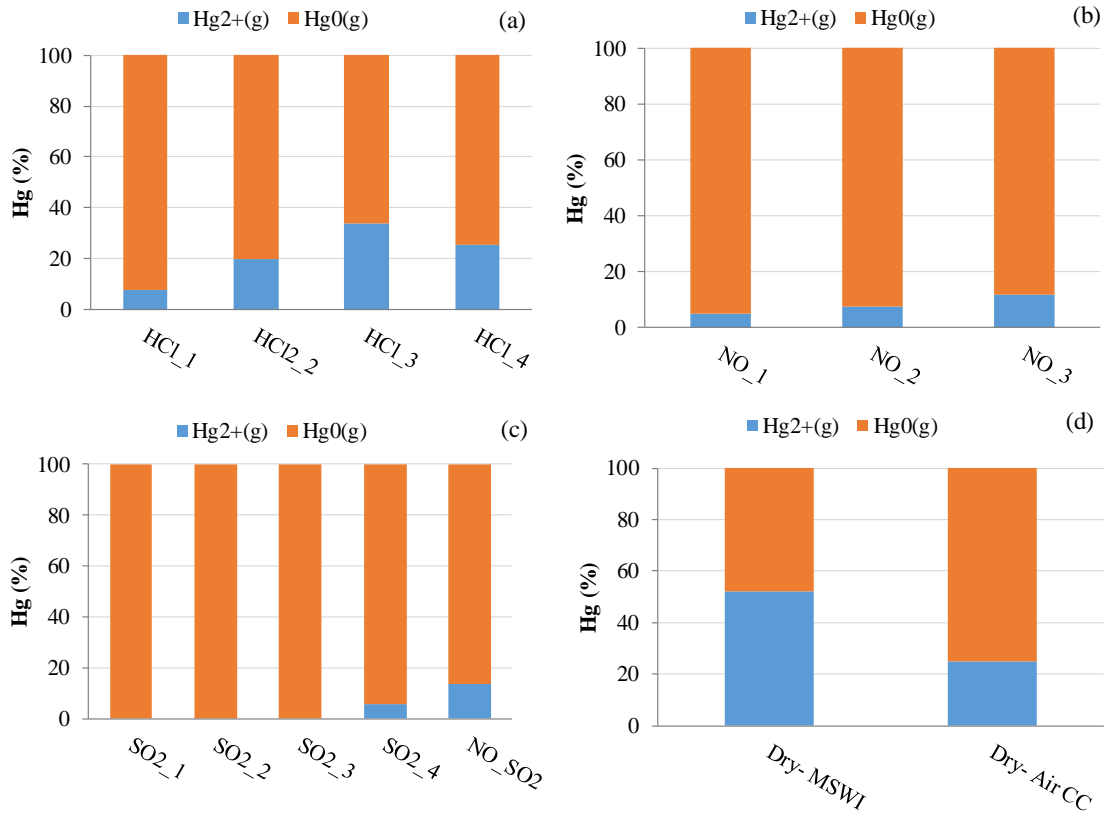
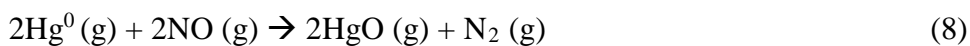


Figure 3. Mercury speciation in gas phase (Hg^0 and Hg^{2+}) under different flue gas composition (Table 1).

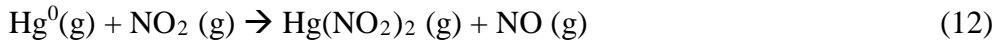
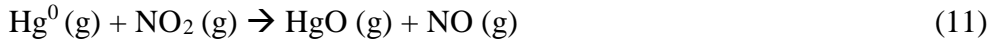
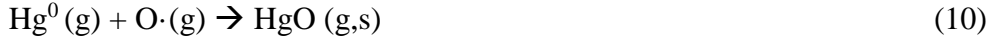
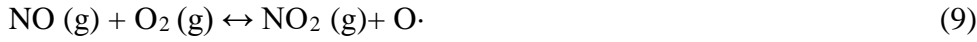
Influence of NO. Figure 3(b) shows that NO has a clear influence on Hg oxidation. 5.0% and 7.5% of Hg^{2+} (g) were obtained in atmospheres of NO balanced with N_2 (with content of NO of 200 and 400 ppm, respectively).

Fernandez-Miranda *et al.* (2014) demonstrated that reaction (8) occurs in similar conditions to the present study.



When both CO_2 and O_2 were present in the gas mixture (NO_3), the percentage of Hg^{2+} (g) increased up to 14%. NO may react with O_2 and it generates NO_2 and radical oxygen atoms (reaction 9), both of them have strong oxidative properties (reactions 10

and 11) (Zhang *et al.*, 2017). NO and NO₂ in oxygen containing atmosphere can react with Hg⁰ vapours to form Hg(NO₂)₂ (e.g. according to reaction 12) and Hg(NO₃)₂.

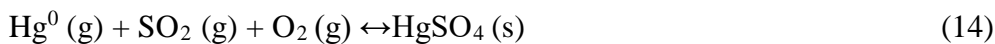


Influence of SO₂. The results obtained in this study show that SO₂ could present either oxidation or inhibitory effect on Hg oxidation. No reaction was found between SO₂ and Hg in the case of N₂+SO₂ atmospheres (SO2_1-3). It was demonstrated, when 5% of O₂ was added to the atmosphere (SO2_4), that the percentage of Hg²⁺ (g) increased to 5.5%.

Fernandez-Miranda *et al.* 2014 demonstrated the occurrence of reaction (13) in atmospheres that simulated flue gas compositions similar to air-combustion and oxy-fuel combustion processes:



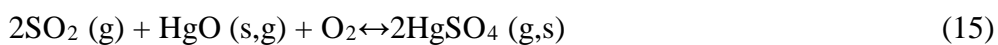
The formation of HgSO₄ in gas phase (14,15) is also possible. However, it is known that there is a high activation energy barrier (Hall *et al.*, 1991).



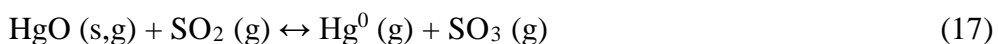
The reaction (14) could be favoured on a suitable surface at sufficiently high temperature but there is no evidence under the conditions of the present section (gas-gas interaction at 150 °C).

It is also suggested that higher percentage of O₂ has a suppressing effect in the homogeneous Hg oxidation by SO₂ because of the competitive formation of SO₃ (16).

SO₃ formed in flue gas is known to be responsible for low temperature corrosion in cold parts of the flue gas cleaning lines (Spörl *et al.*, 2014).



Mercury oxidation in the complex (model flue gas) mixtures. In the atmosphere composed of 10 vol. % CO₂, 5 vol.% O₂, 600 ppm-v HCl, 300 ppm-v SO₂ and 200 ppm-v NO (labelled as MSWI flue gas), the percentage of Hg²⁺(g) obtained was 52%. A Hg²⁺(g) percentage of 25% was obtained in the model atmosphere labelled as Air-CC. This oxidation ratio was much lower than that resulted in MSWI model flue gas. Air-CC atmosphere composed of 10 vol. % CO₂, 5 vol.% O₂, 30 ppm-v HCl, 1000 ppm-v SO₂ and 1000 ppm-v NO. It differs mainly in its significantly lower content of HCl and higher content of SO₂ and NO with respect to MSWI model flue gas composition. NO, SO₂ and HCl exhibited a synergy-like effect in the extent of mercury gas oxidation. Nevertheless, both SO₂ and NO displayed lower oxidizing capabilities than gaseous HCl. The higher HCl content, the higher mercury oxidation rate (it means oxidation of Hg in MSWI > Air-CC). High content of SO₂ could lead to formation of SO₃ (H₂SO₄) in detriment of mercury oxidation. A parallel reaction (17) would reduce Hg²⁺(g) to Hg⁰ (g) at the same time. This fact is the explanation why under air-coal combustion conditions (Air-CC), the oxidation extent is much lower (25%) than under simulated MSWI conditions (52%) despite its higher content of NO (1000 ppm-v) and SO₂ (1000 ppm-v) in comparison with those corresponding with MSWI atmosphere (300 ppm-v of SO₂ and 200 ppm-v of NO).



A simulation of the Hg species formed in the complete atmospheres (MSWI and Air-CC) was done by means of HSC Chemistry 7.0 (Figure 4). The predictions are based only on

thermodynamic data, discarding kinetics. The obtained results showed a strong influence of HCl in the species formed. Clearly, HgCl_2 is the main Hg compound formed under the conditions of dry MSWI atmosphere used the study (with 600 ppm-v of HCl). However, in the case of Air-CC atmosphere, where HCl is a minor compound in the flue gas (30 ppm-v), the obtained distribution of species completely changed, being HgO most likely to be form as main Hg species in the flue gas atmosphere.

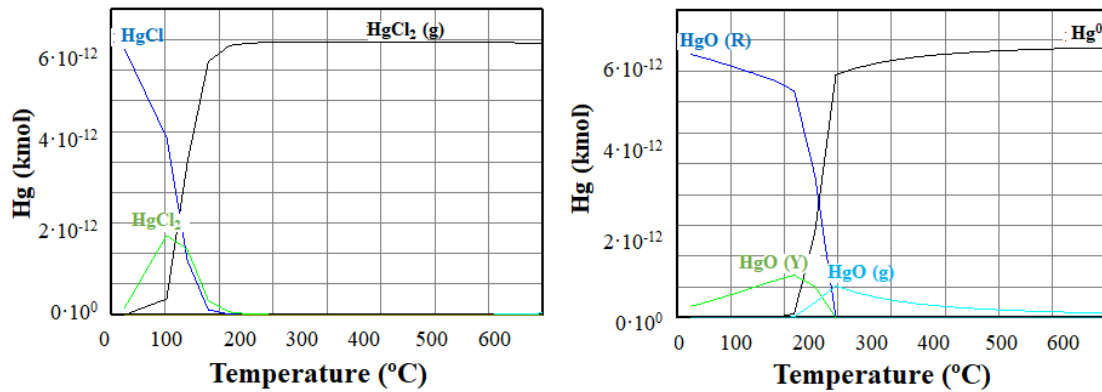


Figure 4. Thermodynamic diagrams obtained by HSC Chemistry using the complete atmospheres: (a) *MSWI* flue gas and (b) *Air-CC* flue gas.

3.2. Mercury heterogeneous oxidation study

Important factors that strongly influence the oxidation extent, speciation and removal of Hg from flue gas in incineration facilities are the composition and properties of the fly ashes (generated in the waste incineration and gas cleaning process). In this study, heterogeneous oxidation and capture of Hg was evaluated in presence of three fly ash samples collected from a WtE plant in the Czech Republic. Series of Hg-removal/sorption experiments in presence of the FA1, FA2 and FA3 samples were carried out in the fixed-bed experimental device using atmospheres of N₂, simulated Air-CC and MSWI flue gas. The Hg⁰(g) removal efficiency was evaluated as a function of time (during 300 min) at

150°C. The $\text{Hg}^0(\text{g})$ concentrations at the outlet of the reactor were continuously measured with the mercury analyser (VM3000). The $\text{Hg}^{2+}(\text{g})$ downstream the fixed bed reactor was extracted from the gas stream by the Hg^{2+} -selective resin (Dowex) placed downstream the gas outlet of the reactor and upstream the Hg^0 vapour analyser. The Hg^{2+} is derived from both homogeneous oxidation (gas-gas interaction) and heterogeneous oxidation (gas-sorbent interaction). Content of mercury captured by the fly ash (Hg_{cap}) and the Hg^{2+} (captured by the resin) were determined by the automatic analyser AMA254. Figure 3 displays the results of Hg^0 removal capacity obtained in presence of FA1 and FA2. The graphics exhibit two lines (Homogeneous Air-CC and Homogeneous MSWI mercury oxidation extent) corresponding to the percentage of mercury oxidized by the gas-gas interactions in each gas atmosphere. The curves corresponding to inert atmosphere (N_2) represent the capacity of the fly ash samples to either capture Hg or oxidize/capture Hg, because no interactions occur due to the presence of reactive-gaseous compounds (gas-gas interactions). FA1 achieved 12% removal capacity in 8 min and remained constant during 300 min. The removal capacity of FA2 in 10 min was 19% and it was slightly descending with time up to 14% in 300 min. It has been demonstrated that carbon content (or presence of carbon particles) is a key factor in the capture of Hg^0 via physical adsorption (Zhao *et al.*, 2010). Besides the carbon particles, the content and participation of chlorine cannot be ruled out. FA1 and FA2 have 1% and 2.1% of unburnt carbon content and 0.3% and 1.4% of chlorine content, respectively. The proposed mechanism is based on Mars-Maessen mechanism (18-19):



HgCl₂ adsorbed in the chlorinated-carbon sites would be partly desorbed again into the gas stream (20) due the thermal instability of this compound in the range of usual temperatures in flue gas cleaning lines (Rumayor, 2013). In addition, it was found that the oxidation and adsorption activities depends on the metallic element of chloride in the order CuCl₂ > FeCl₃ > MnCl₂ > CeCl₃ > CoCl₂ (Xu *et al.*, 2013).

The results obtained demonstrated that the Hg⁰ removal capacity is effectively correlated with the unburnt carbon content and chlorine content of the fly ash. The results using FA1 sample showed that this fly ash has a little effect in the removal efficiency when reactive gaseous compounds were present in the atmospheres (Air-CC or MSWI). It can be seen in Figure 5(a) that the efficiency curves corresponding to each atmosphere (FA1 (Air-CC) and FA1 (MSWI)) are very close to the belonging lines of homogeneous oxidation extent. Only around 4% of the overall Hg⁰ removal is owing to the fly ash (FA1) in both atmospheres. Similar improvement (6%) was found when FA2 was tested under Air-CC atmosphere (Figure 5(b)). However, FA2 sample achieved an improvement of 18% in the overall Hg⁰ efficiency in MSWI flue gas. These results demonstrate the effect of SO₂ which is higher in Air-CC than MSWI. SO₂ would form SO₃ that competes with Hg for the same adsorption binding sites.

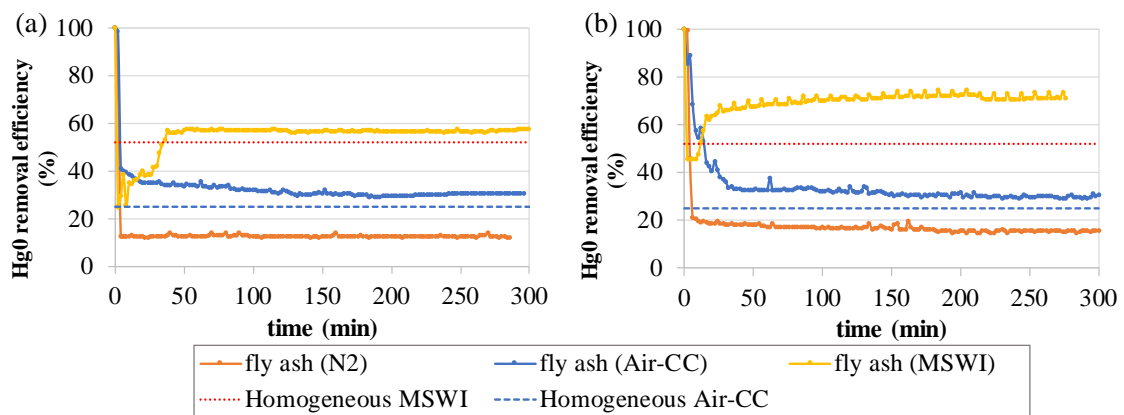


Figure 5. Hg^0 removal efficiency curves in presence of fly ash sample FA1 (a) and fly ash sample FA2 (b) in three atmospheres: N_2 , model Air-CC and MWSI flue gas.

The Hg -sorption results were completely different when FA3 sample was subjected to the Hg^0 removal tests (Figure 6). The fly ash FA3 was able to remove up to 20% of Hg^0 in 300 min when there was no presence of reactive gas compounds (N_2 atmosphere). In the case of Air-CC atmosphere, the removal efficiency was 100% up to 100 min of the sorption time and then the efficiency gradually declined to 72% at a sorption time of 300 min. The probable reason lies in the depletion of active centres for Hg -oxidation and Hg -capture (competition and occupation of the centres by other species). Under conditions of simulated MSWI dry flue gas, the Hg -removal efficiency remained at practically 100% during the sorption time (300 min). These findings show again the effects of high content of SO_2 and HCl on the Hg -removal efficiency. As it was already remarked, the higher content of SO_2 , the higher formation of SO_3 that competes with Hg for the same adsorption binding sites.

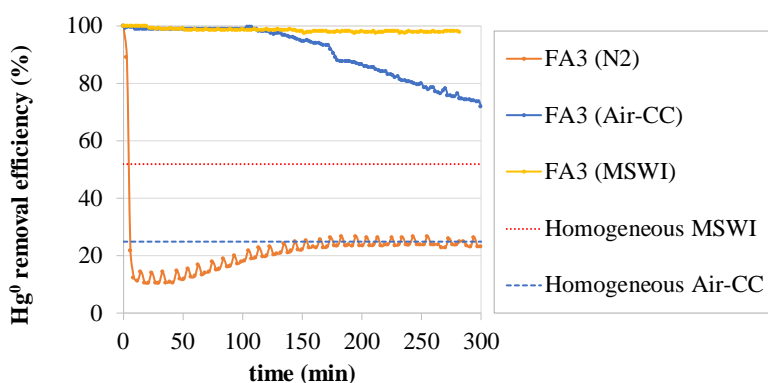
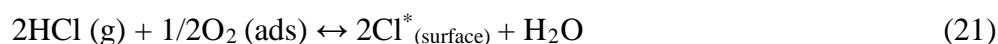


Figure 6. Hg^0 -removal efficiency curves of fly ash sample FA3 in three atmospheres: N_2 , Air-CC and MWSI.

Figure 7 shows the comparison of the amounts of mercury captured by FA1, FA2 and FA3 (during 300 min) in the three atmospheres used in the present study. FA1 and FA2 displayed similar results, having FA2 slightly better characteristics for mercury retention. The main difference between the results of both samples is the low retention capacity of FA1 in N₂ atmosphere. It was expected, as it is the fly ash with lowest content of chlorine (0.3%) and unburnt carbon content (1.0%). In contrast to the samples FA1 and FA2, the fly ash sample FA3 exhibited the best sorption properties for mercury, confirmed by its supreme properties/characteristics: BET specific surface (2.42 m²·g⁻¹), chlorine content (4.75 mass %) and unburnt carbon content (2.7%). The gas atmosphere, labelled as MSWI, favours both mercury oxidation and capture. Because it is the atmosphere with the highest HCl concentration, the oxidation extent in gas phase is higher than the other two atmospheres and furthermore, HCl favours the chlorination of carbon active sites (21), which could increase the number of active centres and Hg capture at the same time (18-19).



Another Hg species likely to be adsorbed on fly ash is HgO. HgO can be either formed in gas phase (gas-gas interactions) and afterwards adsorbed by the fly ash or it can be formed due to the heterogeneous oxidation in the surface and then captured by the fly ash (22-23).



It can be observed that the gas atmosphere corresponding to Air-CC exhibited a clear declination in the capture of mercury. SO₂ affected negatively the removal of Hg, demonstrating that SO₂ competes with Hg⁰ and O₂ for the same adsorption active sites.

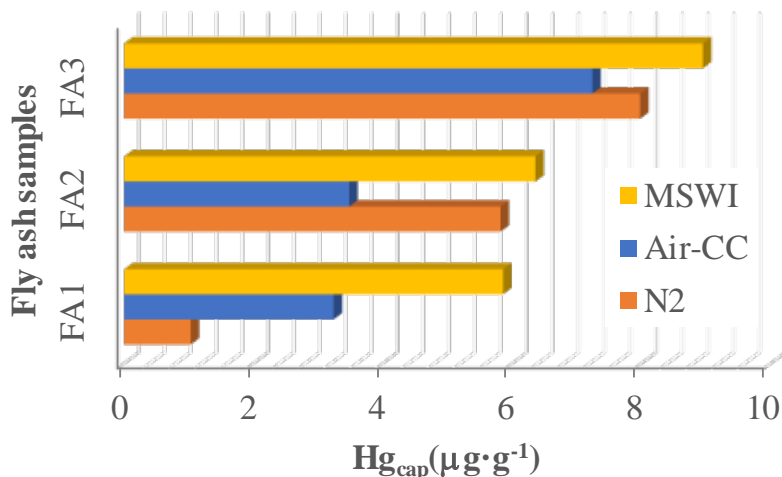


Figure 7. Mercury captured by fly ash samples (FA1, FA2 and FA3) under conditions of model atmospheres of N₂, Air-CC and MSWI flue gas.

4. Conclusions

The results obtained confirm that the typical gas components in MSWI flue gas such as SO₂, NO and HCl have a synergetic effect in Hg-oxidation in presence of O₂. This study confirms that HCl is the main flue gas component responsible for the extent of Hg-homogeneous oxidation in typical flue gas from MSWI. SO₂ can inhibit mercury oxidation and its subsequent capture by fly ash when it is present in higher proportions than HCl, such as in a typical atmosphere of coal combustion flue gas. Fly ashes hardly retained mercury but they exhibited exceptional capacities for mercury oxidation and mitigation of Hg⁰ emissions from the stack. Unburnt carbon content, chlorine content and high specific surface area of fly ash are important factors for attaining reliable mercury capture efficiency. HgCl₂ and HgO are likely species to be adsorbed by fly ash. HgCl₂ would be partly desorbed into the flue gas due to its instability, contributing afterwards to mercury heterogeneous oxidation. HCl could promote the adsorption of mercury due to the chlorination of the fly ash surface, generating more active centres for Hg capture.

Acknowledgments

The authors appreciate financial support provided by the Technology Agency of the Czech Republic (TA CR), project Centre of Competence Waste to Energy, TE02000236.

The authors thank to the Academy of Sciences of the CAS, v.v.i., Prague for awarding Dr Marta Rumayor the PPLZ support of foreign scientific workers. Authors thank to Dr. Jan Kratzer from the Department of trace element analysis of the Institute of Analytical Chemistry of the CAS, v. v. i. for allowing us to perform the mercury analytical determination in solid samples.

References

Cheng, H. and Hu, Y., 2012. Mercury in municipal solid waste in China and its control: a review, *Environ. Sci. Technol.*, 46, 593-605.

H. Deacon, US Patent 165, 802 (1875).

Fernández-Miranda, N., López-Antón, M.A., Díaz-Somoano, M., Martínez-Tarazona, M.R., 2014. Effect of oxy-combustion flue gas on mercury oxidation. *Environ. Sci. and Technol.* 48(12), 7164-7170.

Fuente-Cuesta, A, Díaz-Somoano, M., López-Antón, M.A., Martínez-Tarazona, M.R., 2014. Oxidised mercury determination from combustion gases using an ionic exchanger, *Fuel.* 122, 218-222.

Gasper, J.A., Widmer, N.C., Cole, J.A., Seeker, W.R., 1997. Study of mercury speciation in a simulated municipal waste incinerator fuel gas. In: *Proceedings of the International Conference on Incineration and Thermal Treatment Technologies.* Oakland, California Univ. Office of Environment, Health & Safety.

Hall, B., Lindqvist, O., Ljungström, E., 1990. Mercury chemistry in simulated flue gases related to waste incineration conditions. *Environ. Sci. Technol.* 24, 108-111.

Hall, B., Schager, P., Lindqvist, O., 1991. Chemical-Reactions of Mercury in Combustion Flue-Gases. *Water Air and Soil Poll.* 56, 3-14.

He, P., Zhang, X., Peng, X., Wu, J., Jiang, X., 2016. Effect of fly ash composition on the retention of mercury in coal-combustion flue gas. *Fuel Process. Technol.* 142, 6-12.

Hranisavljevic J. and Fontijn A., 1997. Kinetics of Ground-State Cd Reactions with Cl₂, O₂, and HCl over Wide Temperature Ranges, *J. Phys. Chem.* 101, 2323-2326.

López-Antón, M.A., Abad-Valle, P., Díaz-Somoano, M., Suárez-Ruiz, I., Martínez-Tarazona, M.R., 2009. The influence of carbon particle type in fly ashes on mercury adsorption. *Fuel.* 88 (7), 1194-1200.

Naruse, I., Yoshiie, R., Kameshima, T., Takuwa T., 2010. Gaseous mercury oxidation behavior in homogeneous reaction with chlorine compounds *J Mater Cycles Waste Manag.* 12, 154-160.

Niksa, S., Helble, J.J., Fujiwara, N., 2001. Kinetic modeling of homogeneous mercury oxidation: the importance of NO and H₂O in predicting oxidation in coal. *Environ Sci. Technol.* 35, 3701-3706.

Niksa, S., Padak, B., Krishnakumar, B., and Naik, C.V., 2010. Process chemistry of Br addition to utility flue Gas for Hg emissions control. *Energy Fuels* 24, 1020-1029.

Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson., E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A., 2003. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Process. Technol.* 82, 89-165.

- Riber, C., Petersen, C., Christensen, T.H., 2009. Chemical composition of material fractions in Danish household waste, *Waste Manage.* 29, 1251-1257.
- Rumayor, M., Díaz-Somoano, M., López-Antón, M.A., Martínez-Tarazona, M.R., 2013. Mercury compounds characterization by thermal desorption, *Talanta* 114, 318-322.
- Senior, C.L., Sarofim A.F., Zeng, T., Helble, J.J., Mamani-Paco, R., 2000. Gas-phase transformations of mercury in coal-fired power plants. *Fuel Process. Technol.* 63, 197-221.
- Sliger, R.N., Kramlich, J.C., Marinov, N.M., 2000. Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species, *Fuel Process. Technol.* 65-66, 423-438.
- Spörl, R., Maier, J., Belo, L., Shah, K., Stanger, R., Wall, T., Scheffknecht, G., 2014. Mercury and SO₃ Emissions in Oxy-Fuel Combustion. *Energy Procedia* 63, 386-402.
- Svoboda, K., Hartman, M., Šyc, M., Pohořelý, M., Kameníková, P., Jeremiáš, M., Durda T., 2016. Possibilities of mercury removal in the dry flue gas cleaning lines of solid waste incineration units (Review) *J. Environ. Manage.* 166, 499-511.
- Sysalová, J., Kučera, J., Fikrle, M., Drtinová, B., 2013. Determination of the total mercury in contaminated soils by direct solid sampling atomic absorption spectrometry using an AMA-254 device and radiochemical neutron activation analysis. *Microchem. J.* 110, 691-694.
- United Nations Environment Programme (UNEP). Minamata Convention on Mercury. http://www.mercuryconvention.org/Convenio/tabid/5690/language/es_CO/Default.aspx/, 2013 (accessed 13.06.17).

Van Veizen, D., Langenkamp, H., Herb, G., 2002. Review: mercury in waste incineration, *Waste Manag. Res.* 20(6), 556-568.

Waldner, M.H., Halter, R., Sigg, A., Brosch, B., Gehrman, H.J., Keunecke, M., 2013. Energy from waste – clean, efficient, renewable: transitions in combustion efficiency and NO_x control, *Waste Manag.* 33, 317-326.

Widmer, N.C., Cole, J.A., Seeker, W.R., Gaspar, J.A., 1998. Practical limitation of mercury speciation in simulated municipal waste incinerator flue gas *Combust. Sci. Technol.* 134, 315-326.

Widmer, N.C., West, J., Cole, J.A., 2000. Thermochemical study of mercury oxidation in utility boiler flue gases. In: *Proceedings of the A&WMA Annual Conference.* AWMA, Pittsburgh.

Schroeder W.H and Munthe J., 1998. Atmospheric mercury—An overview, *Atmos. Environ.*, 32 (5), 809-822.

Xu, M., Qiao, Y., Zheng, C., Li, L., Liu, J., 2003. Modeling of homogeneous mercury speciation using detailed chemical kinetics. *Combust. Flame.* 132, 208-218.

Xu, W., Wang, H., Zhu, T., Kuang, J., Jing, P., 2013. Mercury removal from coal combustion flue gas by modified fly ash. *J. Environ. Sci.*, 25 (2), 393-398.

Yang, Y., Liu, J., Shen, F., Zhao L., Wang, Z., Long, Y., 2016. Kinetic study of heterogeneous mercury oxidation by HCl on fly ash surface in coal-fired flue gas. *Combust. Flame* 168, 1-9.

Zhang, H., He, P.J., Shao, L.M., 2008. Fate of heavy metals during municipal solid waste incineration in Shanghai, *J. Hazard. Mater.* 156, 365-373.

Zhang, Y., Zhao, L., Guo, R., Wang, J., Cao, Y., Orndorff, W., Pan, W., 2017. Influences of NO on mercury adsorption characteristics for HBr modified fly ash. *Int. J. Coal Geol.* 170, 77-83.

Zhao, Y., Zhang, J., Liu, J., Díaz-Somoano, M., Martínez-Tarazona, M.R., Zheng C., 2010. Study on mechanism of mercury oxidation by fly ash from coal combustion. *Chin Sci Bull*, 55, 163-167.