



Research article

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



M. Rumayor^{a, b, *}, K. Svoboda^{a, c}, J. Švehla^a, M. Pohorelý^a, M. Šyc^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 Výchova 7, 400 96, Ústí nad Labem, Czech Republic

ARTICLE INFO

Article history:

Received 2 August 2017

Received in revised form

9 October 2017

Accepted 19 October 2017

Keywords:

Mercury

Waste to energy

Oxidation

Fly-ash

Capture

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 (O₂, HCl, SO₂ and NO). Series of model, synthetic dry flue gases were used to elucidate the effects of HCl, SO₂, NO and their proportions in the gas on mercury behaviour. Three samples of fly ash collected from a MSWI 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 ± 5% and 25%, respectively. SO₂, 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 SO₂. 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 m²/g) was able to remove up to 100% of Hg⁰ (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.

© 2017 Elsevier Ltd. All rights reserved.

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 SO₂, 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 Hg⁰ and Hg²⁺ 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 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 et al., 2002).

When elemental mercury (Hg⁰) 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

* Corresponding author. University of Cantabria, Department of Chemical and Biomolecular Engineering, Av. Los Castros s/n, 39005, Santander, Spain.

E-mail addresses: marta.rumayor@unican.es, rumayor@icpf.cas.cz (M. Rumayor).

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 (Fig. 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 Photoelectron 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 Analyser AMA254 (LECO).

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

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 $\text{Hg}^0/\text{Hg}^{2+}$ compounds. The experimental device (Fig. 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 Hg^0 -permeation tube and a Dynacalibrator 150 unit with a thermostat (Valco Instruments Company Inc.) were used for generation of the needed constant concentration of Hg^0 in the flue gas (at the entrance of the tube reactor) of $100 \mu\text{g m}^{-3}$, (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 vapour 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

Download English Version:

<https://daneshyari.com/en/article/7478680>

Download Persian Version:

<https://daneshyari.com/article/7478680>

[Daneshyari.com](https://daneshyari.com)