ANALYSIS OF MERCURY SPECIES PRESENT DURING COAL COMBUSTION BY THERMAL DESORPTION

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Abstract

Mercury in coal and its emissions from coal-fired boilers is a topic of primary environmental concern in the United States and Europe. The predominant forms of mercury in coal-fired flue gas are elemental (Hg^0) and oxidized (Hg^{2+}, primarily as $HgCl_2$). Because Hg^{2+} is more condensable and far more water-soluble than Hg^0, the wide variability in mercury speciation in coal-fired flue gases undermines the total mercury removal efficiency of most mercury emission control technologies. It is important therefore to have an understanding of the behaviour of mercury during coal combustion and the mechanisms of mercury oxidation along the flue gas path. In this study, a temperature programmed decomposition technique was applied in order to acquire an understanding of the mode of decomposition of mercury species during coal combustion. A series of mercury model compounds were used for qualitative calibration. The temperature appearance range of the main mercury species can be arranged in increasing order as $HgCl_2<HgS<HgO<HgSO_4$. Different fly ashes with certified and reference values for mercury concentration were used to evaluate the method. This study has shown that the thermal decomposition test is a newly developed efficient method for identifying and quantifying mercury species from coal combustion products.

1. Introduction

Mercury is considered a dangerous heavy metal to both humans and the ecosystem because it is highly toxic to the central nervous system and it tends to bio-accumulate in the human body. Coal fired power plants are one of the main sources of mercury emission to the environment [1]. As a consequence, legislative bodies both in Europe and USA are considering the reduction of mercury emissions from coal fired power plants an important priority [2-5]. According to a ruling announced in USA, mercury emissions from utility boilers must be reduced to a final cap of 15 ton/year by 2018, equivalent to nearly 70 percent reduction [6].

During combustion, the mercury in the coal is transformed into three species: (i) particle-bound mercury (Hg_p); (ii) vapour-phase elemental mercury (Hg^0) and (iii) vapour-phase oxidized mercury (Hg^{2+}), primarily in the form of $HgCl_2$. For the optimal removal of mercury from flue gas a high level of oxidation is beneficial since, unlike Hg^0, $HgCl_2$ is water soluble which makes its removal in wet flue gas desulphurisation units (FGD) possible. Particle-bound Hg_p is easily removed by dust control equipment such as baghouse filters and electrostatic precipitators (ESPs) [7-8]. Therefore, the conversion of mercury from one form to another is important for selecting the appropriate mercury removal technology.

Hg^0 may be oxidized to Hg^{2+} via homogeneous (gas-gas) or heterogeneous (gas-solid) reactions [9]. Mercury in coal begins to volatilize at temperatures below 200°C almost regardless of the mode of occurrence of mercury in the coal. At temperatures above 600-700°C, Hg^0 is the only stable form [10]. At temperatures <400°C and in the presence of chlorine, part of the Hg^0 vapour is oxidized to $HgCl_2(g)$ by direct reaction of atomic chlorine Cl with elemental mercury [11]. According to the equilibrium reactions model proposed by Frandsen et al., [12] $HgSO_4(s)$ and $HgO(s)$ also become

thermodynamically stable species in conventional coal combustion systems at low temperatures (110-320ºC). A theoretical assessment of the equilibrium composition of mercury-containing species over the 100-1600ºC range in a combustion atmosphere without chlorine indicated that Hg(g) is the most abundant species in gas phase with the presence of small amount of HgO(g), the exact proportions of these two species varying with temperature [13].

The oxidation of mercury depends on the composition of the flue gas and especially on the quantity of HCl, NO_x and SO_2 present [14]. Furthermore, an increase of mercury oxidation has been observed in systems equipped with selective catalytic reduction (SCR) units for NOx control [15].

Experimental evidence suggests that fly ash is able to catalyze the oxidation of elemental mercury [16-22]. Although the role of inorganic components of fly ashes in mercury speciation is still unclear, iron oxide, aluminosilicates and calcium oxide seem to be the main promoters of this oxidation [17, 18, 20].

In order to understand the behaviour of mercury from combustion processes and its range of oxidation, it is important to identify which mercury species are associated with coal combustion products. A method employed to speciate mercury in solid samples is thermally induced desorption. This method has been applied to identify mercury compounds in soil contaminates, sediment samples, iron-based sorbents [23-25] and even in mercury lamp wastes [26]. However, there is a lack of a similar knowledge concerning the speciation of mercury in coal combustion products [27]. Feng et al. [28] identified and quantified different mercury species (Hg^0, $HgCl_2$, HgS and HgO) in airborne particulate matter. The study showed the presence of 23% $HgCl_2$ and 40% HgO, suggesting effluence of industrial processes to the sampling site. Milobowski et al. [29] conducted a similar type of study on samples from wet flue gas

desulfurization processes. They tested samples made up of pure mercury compounds and obtained distinct thermal decomposition curves for four pure mercury compounds. However, it was difficult to distinguish between HgS and HgO in samples containing more than one compound because the thermal decomposition curves overlapped each other. Moreover, there was no attempt to quantify the results of this work. Accordingly, the goal of this study was to develop an experimental method for better identifying the thermally induced behaviour of the main mercury species in coal combustion products. This work will form a useful basis for subsequent studies on the mercury oxidation mechanism in fly ashes and will help to improve mercury removal in coal-fired power plants.

2. Experimental

To study mercury speciation and the assignment of different mercury species to specific anions, a commercially available thermal dissociation module (PS Analytical Thermogram model 50.042) coupled to a mercury analyser (PS Analytical Sir Galahad Mercury Analyser model 10.525) was used. The Sir Galahad mercury analyser employs an atomic fluorescence detector which is specific for Hg^0 and is able to measure (in continuous real-time mode) mercury at a mass flow as low as 1 ng/minute. The mercury compounds present in the sample are carried through the oven tube in a stream of argon, at a flow rate of 250 ml min^{-1}. The commercial unit was modified to improve the temperature distribution along the work-tube between the programmed dissociation furnace and the "cracker" furnace, where the volatilized mercury compounds are fully dissociated prior to detection as elemental mercury. The heating rate from room temperature to 650°C is nominally 10°C min^{-1}.

A number of pure mercury compounds ($HgCl_2$, HgS, $HgSO_4$, HgO, Hg_2Cl_2, Hg_2SO_4, $HgBr_2$) were tested to determine their specific thermograms in order to obtain a set of "fingerprints" which could serve as a standard of comparison for the profiles obtained from the coal combustion products. The content of mercury in the samples was approximately between 1.0-3.0 µg. The pure mercury compounds were diluted using silica flour as inert material. Origin 6.0 professional software was used to deconvolute overlapping peaks of thermal decomposition curves.

The calibration test was performed using a PS Analytical CAVKIT dynamic dilution unit. The CAVKIT unit works on the principle of diluting a saturated mercury vapour at known temperature which provides a known concentration of mercury in a stream of argon at a known flow rate. This results in a final concentration of mercury presented to the analyser of range 5 – 500 ng/L. A standard fly ash (NIST 1633 b) and two reference fly ashes (FA1 and FA2) were used in this study to verify the quantitative analysis. The mercury content in FA1 and FA2 samples was analysed using a cold vapour atomic absorption (CVAA) spectrophotometer.

In order to improve our understanding of the behavior of mercury species, thermodynamic equilibrium models were used in order to predict the composition of the chemical species in the gas phase using the HSC-Chemistry 5.0 software.

3. Results and discussion

3.1. Studies of single pure compounds

The thermograms obtained from the mercury standards $HgCl_2$, Hg_2Cl_2, HgS, HgO, $HgSO_4$, Hg_2SO_4, $HgBr_2$ are shown in Figure 1. The compounds chosen initially were $HgCl_2$, HgS, HgO and $HgSO_4$, as they are the most likely species to form during

coal combustion and in a wet scrubber environment.[29] Apart from chloride, other halogens, such as bromide, have been found in the effluent during coal combustion [30]. This might influence the behaviour of the mercury during the process and for this reason $HgBr_2$ was also included in this study. The results are summarized in Table 1. The following features were observed:

(a) $HgCl_2$ (Figure 1a). The decomposition of this mercury phase occurs at low temperatures ranging from 70 to 220ºC (maximum at 120ºC).

(b) Hg_2Cl_2 (Figure 1a). Two peaks appear within the approximate range 60 to 220ºC with their maxima at 80 and 130ºC, respectively. As already mentioned in other works [26] these two peaks are probably related to the decomposition of Hg_2Cl_2 in two steps:

$$Hg_2Cl_2 \rightarrow Hg^0 + HgCl_2$$

$$HgCl_2 \rightarrow Hg^0 + Cl_2$$
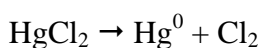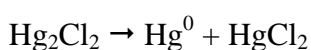
As can be observed the decomposition temperature for the second peak of Hg_2Cl_2 is close to the temperature found for $HgCl_2$ (120^oC)

(c) $HgBr_2$ (Figure 1a). This presents a sharp peak at approximately 110ºC.

(d) HgS (Figure 1b). There are two different HgS crystalline structures: black HgS or metacinnabar and red HgS or cinnabar. Metacinnabar decomposes approximately between 170 and 290ºC with two small peaks appearing at the top at 200 and 250ºC. This fact suggests that metacinnabar starts to decomposition at 200 ºC but its completely decomposition is at 250ºC in the experimental conditions of this study. Cinnabar decomposes at a higher temperature (310ºC) compared with metacinnabar. The thermal desorption curves for metacinnabar and cinnabar are similar to those found in other studies [25]. The structure of cinnabar is trigonal with Hg arranged on a

rhombohedral lattice whereas the structure of metacinnabar is cubic. Mercury release temperatures for mercury suphides may vary slightly due to different crystallinity [24].

(e) Hg_2SO_4 (Figure 1b). The thermal decomposition of this mercury species, unlike the other mercury model compounds, shows a broad signal over the range 120 to 480ºC which sharpens and peaks at 280ºC.

(f) $HgSO_4$ (Figure 1c). This curve presents a pronounced shoulder, extending from 300 to 450ºC with a sharply defined peak at 540ºC.

(g) HgO (Figure 1c). A maximum peak appears at approximately 500ºC with a smaller peak at about 325ºC.

Considering that different heating rates and carrier gas flow rates are employed by individual workers and therefore, variances in the thermal desorption can be observed, the order of the mercury appearance temperatures can be considered similar to those found by Feng et al [28] in matrices of fly ashes ($HgCl_2 < HgS < HgO$). This order suggests that the thermal release of mercury species is related to the vapour pressure [23,28]. When the vapour pressure decreases, the mercury release temperature increases.

In order to confirm the decomposition of different mercury species, a theoretical study was carried out using argon atmosphere as employed in the experiments, and using thermodynamic data at the equilibrium. Figure 2 shows two examples of the thermodynamic analysis. When the $HgSO_4$ is heated in an inert atmosphere, the $HgSO_4$ starts to decompose at 300ºC and finishes decomposing at 700ºC (Figure 2a). Possibly for this reason the fingerprint of this compound (Figure 1c) showed a pronounced shoulder. According to the thermodynamic equilibrium data, $HgSO_4*HgO$ may also form when $HgSO_4$ is heated, in which case it would remain stable only until 600ºC (Figure 2a) and this agrees with the experimental results of thermal decomposition

(Table 1). The thermodynamic studies show that HgO is totally decomposed by approximately 550ºC (Figure 2b) for both the yellow (Y) and red (R) forms. The experimental results again agree with the theoretical studies, as the thermo-decomposition of HgO took place in the 430-560ºC temperature interval (Table 1) The difference between these two compounds is the crystallite size but unlike the mercury sulphides (cinnabar and metacinnabar), both forms of HgO have the same crystallite structure, and therefore, their thermal decomposition takes place at very similar temperatures (Figure 2b). It must not be forgotten that with this software, although it is possible to calculate thermodynamic equilibrium data, the kinetic phenomena are not taken into account.

3.2. Study of mixtures of model compounds

In order to check for any potential interference or interaction resulting from the thermal release of different mercury species, several mixtures of standards were analyzed (Figures 3-7). Figures 3-5 shows three examples of the thermograms obtained with mixtures of black HgS and $HgSO_4$ at a ratio 2:1, black HgS, $HgSO_4$ and Hg_2SO_4 at a ratio 1:1:1 and black HgS and Hg_2SO_4 at a ratio 1:1 by mercury weight. The three sulphur containing mercury species could be identified and therefore they do not appear to interfere with each other. Only in the case of the first mixture (Figure 3), does the maximum peak of $HgSO_4$ appear to be slightly displaced at about 520ºC. Figure 6 shows the thermogram obtained for the mixture $HgCl_2/Hg_2Cl_2$ (1:1). The peaks for each mercury compound could again be identified (Table 1). As it can be observed in Figure 7, similar expected peak temperatures were obtained from a combination of the four main model compounds, where the order of thermal decomposition was chloride, followed by sulphide, oxide and sulphate. Moreover, overlapping peaks were separated

in these mercury standard mixtures by the origin 6.0 software used. The mercury response signals obtained for each mixture were deconvoluted into individual mercury peaks, which are in agreement with the thermal decomposition temperatures for the individual mercury compounds (Table 1), (e.g. Figure 6). Two peaks (grey dot) correspond to the thermal decomposition of Hg_2Cl_2 whereas the other peak (grey dash) corresponds to $HgCl_2$ (Figure 1a, Table 1).

3.3. Quantitative studies

In addition to the qualitative study of the different mercury species, a quantitative analysis was also carried out. Table 2 shows the quantitative analysis results for the mercury standard mixtures (Figures 3-7). The peak area of each individual mercury peak was computed using the PeakFit programme with a Lorentzian distribution. The presence of broad peaks with overlapping (Figures 5-7) and potential errors incurred due to adjustment of the base line by the Origin program used to calculate the peak area (Figure 4) has only allowed a semi-quantitative analysis of each individual mercury compound (Table 2). The analysis can only be considered quantitative when the mixtures show peaks clearly separated peaks of good fit (Figure 3). Despite this, the measured ratios of the components were reasonably satisfactory (Table 2).

In order to confirm the total mercury content in the samples, a reference material of coal fly ash (NIST 1633b) with a certified value for total mercury and two fly ash samples with a mercury concentration analyzed by means of CVAA were used (Table 3). Although the precision of the quantitative results obtained from the thermal decomposition studies, calculated as standard deviation, is lower than that of CVAA, accurate results were obtained, considering also, the low levels of mercury

concentration in these types of materials. Figure 8 shows the thermograms for NIST 1633b and FA1. Two peaks, ranging from 70 to 300ºC, were obtained suggesting that the main mercury species are Hg-Cl and Hg-S (Table 1). The profile from the sample of coal fly ash (Figure 8b) was deconvoluted in order to clarify the mercury halide and sulphur-containing species (Figure 9). The deconvoluted profile suggests that the main mercury species present in this fly ash would be $HgCl_2$ with also some HgS (metacinnabar) (Table 1). The peaks are slightly displaced to the right indicating that some component(s) of the fly ash could be interfering in the thermal decomposition of some mercury compounds.

4. Conclusions

The thermal decomposition method allows different species of mercury to be identified since each presents a characteristic decomposition temperature. The temperature rate of the mercury species can be arranged in increasing order as $HgBr_2 < HgCl_2 < Hg_2Cl_2 < HgS(black) < Hg_2SO_4 < HgS(red) < HgO < HgSO_4$.

Multiple model compounds within a sample were clearly identified. Therefore, thermal desorption appears to be a viable technique for identifying different mercury species in products from coal combustion.

Programmed thermal dissociation coupled with a mercury analyzer allows quantify small amounts of mercury in fly ashes.

Acknowledgments

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