Speciation of mercury in fly ashes by temperature programmed decomposition

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Abstract

Mercury (Hg) is a toxic trace element which is emitted mostly in gas phase during coal combustion, although some Hg compounds may be retained in the fly ashes depending on the characteristics of the ashes and process conditions. To improve the retention of Hg in the fly ashes a good knowledge of the capture mechanism and Hg species present in the fly ashes is essential. The temperature programmed decomposition technique was chosen to identify the Hg species present in fly ashes obtained from two Pulverized Coal Combustion (PCC) plants and a Fluidized Bed Combustion (FBC) plant. The fly ashes were then used as Hg sorbents in a simulated flue gas of coal combustion and gasification. The Hg compounds found in the fly ash from the FBC plant after elemental mercury retention were mainly HgCl_2 and HgSO_4 . The Hg species present in the two fly ashes from the two PCC plants were HgCl_2 and Hg^0 . The Hg species formed in the coal gasification atmosphere was HgS for all three fly ashes. The only Hg compound identified in the fly ashes after the retention of mercury chloride was HgCl_2 .

Keywords: speciation, mercury, fly ashes

1. Introduction

Hg is a persistent toxic pollutant that accumulates in the food chain [1]. Atmospheric Hg is a global problem with many natural and anthropogenic emission sources [2]. Coal-fired power plants are cited as one of the largest sources of Hg emissions to the environment [3]. As a consequence, legislative bodies in Europe and USA are considering reducing Hg emissions from coal-fired power plants [4-7]. A ruling to regulate Hg emissions from coal-fired power plants was announced in USA in line with the Clean Air Act of March 15, 2005 [7]. The USA regulatory structure for Hg emissions from coal-fired power plants is uncertain following the vacatur of EPA's Clean Air Mercury Rule on February 8, 2008 [8], the U.S. Environmental Protection Agency (EPA), in collaboration with public and private research organizations, has fostered the development of a suite of Hg control technologies for coal-fired power plants [9].

Although various control technologies have been investigated, until now no cost-effective or efficient control process has been developed for Hg removal in coal-fired power stations. Sorbents, such as activated carbons, are considered to be effective sorbents for Hg control in flue gases from coal combustion [10-13]. However, economic alternatives need to be developed. The growing interest in developing Hg capture systems has encouraged several research groups to determine the maximum level of retention that can be achieved by by-products from combustion plants. Recent research has shown that certain fly ash materials have an affinity for Hg and that a number of variables may influence Hg capture by fly ashes [14-21].

The speciation of Hg in fly ashes can provide valuable information for understanding the Hg retention mechanism in these by-products. One of the methods

employed to speciate Hg in solid samples is thermally induced desorption. The thermal desorption method for Hg species takes advantage of the fact that the species can be arranged in increasing order (e.g. $\text{HgCl}_2 < \text{HgS} < \text{HgO} < \text{HgSO}_4$) according to the temperature of desorption [22]. Thermal decomposition has been used to identify Hg compounds in soil contaminants, 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 Hg in coal combustion products [27]. Milobowski et al. [28] conducted a study on samples obtained from wet flue gas desulfurization processes. The samples showed different thermal decomposition profiles. From the first profile, it was difficult to distinguish between HgS and HgO, whereas the second curve corresponded well with HgSO_4 . When the thermal desorption method was employed by Rallo et al. [29-30] to identify Hg species in gypsum from combustion and co-combustion plants several Hg species were identified. The most probable Hg species present in the gypsum samples were mercury sulphate and mercury halogenated compounds [29-30]. Feng et al. [31] showed that Hg^0 , HgCl_2 , HgO, and HgS species exist in airborne particulate matter by means of thermal desorption. They also used the coal fly ash standard NIST 1633b to verify the quantitative analysis and suggested that the main Hg species in this standard was HgCl_2 [31]. In their study on thermal Hg stability in fly ashes, Rubel et al. [32] found a good correlation between the mercury and sulphur contents, suggesting that the Hg may have been deposited on the ash as a sulphur compound. Similar results were found by Lopez-Anton et al. [33], indicating that mercury sulphur compounds were the most probable species present in two fly ashes from different power plants.

In line with previous publications on temperature programmed decomposition [22, 29-30], the aim of the present work is to develop an experimental method for studying the thermally induced behaviour of the main Hg species in fly ashes. The fly ashes were used as Hg sorbents in different flue gas compositions.

2. Experimental

Three fly ash samples (CTA, CTSR, and CTP) were studied. CTA was obtained from a pulverized coal power plant (PCC) that uses a coal blend containing a high rank coal. CTSR was sampled from a PCC plant in which the coal blends contained bituminous coals. The third fly ash (CTP) was taken from a fluidised bed combustion plant (FBC) that burns coal mixtures and coal wastes with a high mineral matter content, and uses limestone in the bed. These fly ashes had been previously employed as sorbents of $\text{Hg}^0(\text{g})$ and $\text{HgCl}_2(\text{g})$ [19, 34]. The Hg species present in the gas atmosphere were obtained by evaporating Hg^0 and HgCl_2 , respectively. Two synthetic gas mixtures, one with a gas composition containing species present in the coal gasification atmosphere (64% CO , 3.7% CO_2 , 20.9% H_2 , 1.0 H_2S , 4.0 H_2O) and the other containing species present in the coal combustion atmosphere (15% CO_2 , 9.2% O_2 , 0.2% SO_2 , 6.6% H_2O) were used in the retention experiments. A schematic diagram of the experimental device is shown in Figure 1. The results obtained in the two simulated flue gases were compared with those obtained in an inert atmosphere of N_2 .

To study the speciation of Hg in the fly ashes post-retention and in order to assign the Hg 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 Hg compounds present in the sample were carried through the oven tube in a stream of argon, at a flow rate of 250 ml min⁻¹. The heating rate from room temperature to 650°C was nominally 10°C min⁻¹ [22, 29-30]. A number of pure Hg compounds (HgCl₂, HgS, HgSO₄, HgO) were first tested in order to determine their specific profiles so as to have a set of “fingerprints” which could serve as a standard of comparison for the profiles obtained from the fly ashes. The pure Hg compounds were diluted using a fly ash free of Hg to simulate the decomposition of Hg species in the fly ash samples.

The Hg content in the fly ashes was determined by means of an Automatic Mercury Analyser (AMA). The sulphur and chlorine contents were determined by an automatic analyser LECO SC-132 and ionic chromatography, respectively.

3. Results and discussion

3.1. Thermal decomposition of mercury pure compounds in a matrix of fly ash

As in previous studies carried out by Lopez-Anton et al. [22], a series of Hg standards was used to determine the specific thermograms of each species. In this study, in order to simulate the real behaviour of Hg in fly ashes, the pure Hg compounds were mixed in a matrix of mercury-free fly ash. Since certain constituents of the fly ash might affect the temperature of decomposition of the Hg species, the Hg standards were mixed with fly ash instead of with silica flour [22].

The compounds chosen were again those species which are most likely to form during coal combustion: HgCl_2 , HgS , HgO , and HgSO_4 [28] (Figure 2). The sample blank-FA corresponds to the fly ash free of Hg and the thermogram obtained does not present any peak (Figure 2). The decomposition of HgCl_2 occurs at temperatures ranging between 50 and 150°C with a maximum peak at approximately 85°C. The next Hg compounds to decompose are the mercury sulphides between 170 and 330°C. As noted by Lopez-Anton et al. [22], there are two different HgS crystalline structures: cubic black HgS or metacinnabar which decomposes at 265°C and trigonal red HgS or cinnabar which decomposes at 290°C [22, 24]. HgO and HgSO_4 decompose at higher temperatures than mercury sulphides. HgO starts to decompose at approximately 200°C, but presents a sharply defined peak at 430°C. The thermal decomposition of HgSO_4 is centered at 570°C.

The results obtained in the matrix of fly ash are summarized in Table 1 together with the results of a previous study for Hg pure compounds prepared in silica flour [22]. The temperatures of decomposition are similar, as are the temperature intervals. The thermal release of HgCl_2 and red HgS in the fly ash matrix occurs at a slightly lower temperature than in the silica matrix, whereas that of HgSO_4 occurs at a slightly higher temperature. Whereas metacinnabar (black HgS) presented two small peaks at 200 and 250°C in the silica matrix [22], in the fly ash matrix it exhibited only one peak with a small shoulder (Table 1, Figure 2). The behaviour of HgO in the fly ash matrix is especially noteworthy because its interval of decomposition is wider than that of the HgO in silica with the maximum peak appearing at a lower temperature (Table 1). This suggests

that the thermal release of HgO may have been influenced by a component or components of the fly ashes.

Although variations in Hg thermal desorption do occur, depending on heating rates and carrier gas flow rates employed, the results of this study confirm the previous findings by Lopez-Anton et al. [22] and Feng et al [31] for fly ashes where the order of Hg desorption temperatures is $\text{HgCl}_2 < \text{HgS} < \text{HgO}$.

3.2. Analysis of mercury species in fly ashes post-retention

In order to confirm the results of the previous studies carried out by Lopez-Anton et al. [19, 34] in which fly ashes were used as sorbents for Hg retention in combustion and gasification atmospheres, the temperature programmed decomposition method was employed to identify the Hg species formed in the different atmospheres. Figures 3-6 show the thermal decomposition profiles of the fly ashes obtained post-retention of Hg^0 and HgCl_2 in inert, combustion and gasification atmospheres. In previous experiments by Lopez-Anton et al. [19] the retention of Hg in fly ashes was greatly influenced by the gas composition. The amount of Hg^0 captured in the gasification atmosphere and in N_2 was similar, the highest capture being achieved in the combustion atmosphere [19]. However, when the source of mercury was HgCl_2 , the retention was similar in all three atmospheres [34].

The thermal decomposition of the Hg compounds in the three fly ash samples after Hg^0 retention in the N_2 atmosphere occurs at a low temperature ranging from approximately 50 to 150 °C (Figure 3). According to the decomposition temperatures for different Hg compounds (Table 1), HgCl_2 should be the main Hg compound present in

the three fly ashes under inert atmosphere. Some of the fly ash components may oxidize Hg^0 to Hg(II) [17, 19], favouring the reaction with the chloride. Table 2 shows the chlorine content together with the sulphur and mercury contents of the fly ashes. The CTP fly ash has a second peak at approximately 580°C, suggesting that HgSO_4 is also present in this fly ash (Figure 3, Table 2). However, the CTP sample was procured from a fluidized bed combustion plant (FBC) using limestone in the bed to retain SO_2 . Fly ash CTP can therefore be expected to show a higher sulphur content (Table 2), explaining why the Hg is present in the form of HgSO_4 in this fly ash (Figure 3). The highest Hg signal corresponds to the CTSR fly ash from the power station that burns mainly bituminous coals and its high chloride content therefore would favour the formation of HgCl_2 (Figure 3; Table 2). CTSR starts to decompose before 50°C, at which point Hg^0 may also be decomposing [31].

The Hg decomposition curve for CTP in the combustion atmosphere is similar to that obtained in the N_2 atmosphere, suggesting that the same Hg species are present in both atmospheres (Figure 4, Table 1). The CTA and CTSR thermograms in the combustion atmosphere display broader and higher peaks than in the N_2 atmosphere in accordance with the results for Hg retention [19]. Again the thermal decomposition of Hg starts before 50°C (Figure 4). Therefore, in addition to HgCl_2 , the presence of Hg^0 cannot be ruled out.

Figure 5 shows the thermograms corresponding to the fly ashes after the retention of Hg^0 in the gasification atmosphere. Desorption of the Hg compounds occurs at temperatures ranging from 150 to 350°C. The temperatures corresponding to the decomposition of mercury sulphides (Table 1) are what one would expect in a

gasification atmosphere containing H_2S . In previous studies [19, 34], it was suggested that the Hg species formed in the N_2 and gasification atmospheres were the same because the retention capacities in both atmospheres were similar. However, the results obtained from thermal desorption in this study show that, while Hg is present mainly as HgCl_2 in the N_2 atmosphere (Figure 3), in the gasification atmosphere it is in the form of HgS (Figure 5).

The retention of Hg by these three fly ashes using HgCl_2 as the source of Hg under different atmospheres has also been studied by Lopez-Anton et al. [34]. Hg capture was found to be similar in most of the cases in all of the atmospheres studied. $\text{HgCl}_2(\text{g})$ might, therefore, be expected to be the species retained in the simulated combustion and gasification flue gas and in the inert atmosphere when HgCl_2 is the source of Hg and indeed this was confirmed by thermal decomposition. As an example, Figure 6 illustrates the findings for fly ash CTA. As can be seen, the same Hg compound is present in the N_2 , combustion, and gasification atmospheres. The curves obtained from temperature programmed decomposition between 50-180°C suggest that HgCl_2 is the only species present in the fly ashes studied (Table 1).

4. Conclusions

By employing a temperature programmed decomposition method, it was possible to identify the Hg species present in the different fly ashes studied. The Hg compounds present in the CTP fly ash from the FBC plant after the retention of elemental mercury in N_2 and in a simulated flue gas from coal combustion were mainly HgCl_2 and HgSO_4 . The Hg present in the CTA and CTSR fly ashes from the PCC plant could be HgCl_2 but the

presence of Hg^0 cannot be ruled out. HgS was the Hg species formed in the coal gasification atmosphere in all three fly ashes. HgCl_2 was the only Hg compound identified in the fly ashes after the retention of mercury chloride for all three atmospheres. Thus, in this study, thermal decomposition has proved to be a useful tool for helping to understand the mechanism of Hg retention in fly ashes.

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Captions of Figures

Figure 1. Schematic diagram of the experimental device

Figure 2. Thermal decomposition profiles of model mercury compounds in a matrix of fly ash

Figure 3. Thermal decomposition profiles of fly ash samples in an inert atmosphere

Figure 4. Thermal decomposition profiles of fly ash samples in a coal combustion atmosphere

Figure 5. Thermal decomposition profiles of fly ash samples in a coal gasification atmosphere

Figure 6. Thermal decomposition profiles of CTA fly ash when HgCl_2 is the source of mercury in an inert, combustion, and gasification atmosphere