

Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition

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ABSTRACT

Temperature programmed decomposition was used to identify mercury (Hg) species in gypsum samples produced from flue gas desulfurization in two Spanish power stations (A and B). As stricter emission control/reduction policies, particularly those focusing on Hg, are being implemented, wet flue gas desulfurization (FGD) technologies used for the removal of SO₂ can result in the co-removal of highly-soluble oxidized Hg. The amount of Hg retained in FGD products may increase in the future if these units are optimized for co-capture. For this reason, it is important to identify the mercury species in FGD products not only to determine the potential risk when the wastes are finally disposed of, but also to understand the behaviour of mercury during combustion and therefore to improve the technologies for mercury removal. Different mercury species were identified in the gypsum samples. In power station A, Hg-S were the most probable Hg species, whereas in power station B the main compound was Hg halogenated compounds.

Keywords: mercury; gypsum; coal combustion

1. Introduction

Coal-fired plants have been identified as the largest anthropogenic sources of mercury emissions to the atmosphere [1-2]. The European Commission launched the EU's Mercury Strategy in 2005 [2]. It is a comprehensive plan addressed to mercury pollution which contains 20 measures to reduce mercury emissions, cut supply and demand and protect against exposure [3].

During coal combustion, Hg can be present in different oxidation states, mainly elemental Hg(0) and oxidized [4], and while Hg(0) is volatile, relatively inert and virtually insoluble, Hg(II) is water-soluble. Therefore, wet FGD technologies used for the removal of SO₂ can result in the co-removal of highly-soluble oxidized Hg. For this reason, it is important to understand the chemistry of the Hg-FGD gypsum interaction. The speciation of Hg in gypsum might have an important role in the understanding of Hg behaviour during coal combustion and its mobilization in water and land [5-7]. Chemical speciation methods such as the Ontario Hydro method [8] can give us information on the oxidation state of Hg but not the chemical species. However, Hg species can be identified by temperature programmed decomposition [9-20]. As a continuation of previous studies carried out by the authors [9, 17], the objective of this study is to prove that the thermal decomposition test is an efficient method for identifying mercury species from coal combustion products.

This method has been applied to identify Hg compounds in different type of solid samples [10-14]. However, there is a lack of knowledge concerning the speciation of Hg in coal combustion by-products [15], especially in gypsum samples [16-17]. Milobowski et al. [18] conducted a study on samples from wet flue gas desulfurization processes. The

samples showed two thermal decomposition curves. In the first curve it was difficult to distinguish between HgS and HgO whereas the second curve corresponded well with HgSO₄. Although any of the thermal evolutionary curves obtained from the pure mercury standards did not exactly match with those of the FGD gypsum and wallboard samples, Lee et al.[16] identified that Hg₂Cl₂ and HgCl₂ could be the present species. When the thermal desorption method was used to identify Hg species in gypsum from a co-combustion plant the main species identified was HgCl₂ [17]. Nowadays the use of biomass and systems to reduce NO_x emissions could modify the behaviour of Hg during coal combustion and particularly in the FGD units. Gypsum samples from two Spanish pulverized coal (co) combustion power plants were tested using temperature programmed decomposition to identify different mercury species, leading to better understanding of Hg behaviour and its retention in FGD systems.

2. Experimental

The study was carried out in two 1200 MW Spanish power stations (A and B) equipped with a wet limestone-based with forced oxidation FGD facility. The power plant A burns a coal blend ranging from local sub-bituminous coals (60%) close to lignite to bituminous coals (40%). The power station B burns a blend of anthracites (80%) and petroleum-coke (20%). Gypsum samples were taken from the conveyor belt where the dry gypsum is transported from the FGD unit to collection point. Subsequently the samples were stored in closed containers of polyethylene. Gypsum samples were called FGD-A and FGD-B from power station A and B, respectively.

The experimental device has been described by the authors in previous works [9,17]. It consists of a thermal dissociation rig (PS Analytical Thermogram model 50.042) coupled to a mercury analyser (PS Analytical Sir Galahad Mercury Analyser model 10.525). The commercial thermal dissociation unit was modified to improve the temperature distribution along the work-tube between the programmed dissociation zone (40-650°C max) and the “cracker” zone (operated at 800°C), where the volatilized mercury compounds are fully dissociated prior to detection as elemental mercury by the atomic fluorescence detector. The mercury compounds present in the solid sample are subjected to a programmed rise in temperature of 10°C min⁻¹. A water trap of silica gel was integrated in the system just before the Sir Galahad detector.

Cold Vapour Atomic Fluorescence spectroscopy (CV-AFS) was used to determine the Hg contents in the samples. BET surface area was determined by volumetric adsorption of nitrogen at 77K. “Malvern Mastersizer-S” particle size analyzer was used for the particle size characterization.

3. Results and discussion

The FGD gypsum samples have a moisture content of approximately 20%. Surface area, porosity, particle size and Hg concentration for gypsum samples are presented in Table 1. The Hg concentration in FGD gypsum samples was 0.15 and 0.31 mg kg⁻¹ for power plants A and B, respectively. No significance differences were found in the surface area, porosity and particle size between power station A burning a blend of coals and power station B burning a blend of pet-coke and coal.

According to a previous study carried out by the authors [9], the thermal decomposition method allows the identification of individual Hg compounds as a function of Hg release with temperature. In this previous work the temperature appearance range of the main Hg species was arranged in increasing order as $\text{HgCl}_2 < \text{HgS} < \text{HgO} < \text{HgSO}_4$. They are the most likely species to form during coal combustion and in a wet scrubber environment [18]. Because other halogens, such as HgI_2 can be found in the effluent during coal combustion [7], the thermal decomposition for HgI_2 has been included in this study. Figure 1 shows the thermograms for the studied Hg halogenated compounds. The order of the Hg appearance temperatures can be arranged in increasing order as $\text{HgI}_2 < \text{HgBr}_2 < \text{HgCl}_2$. This order suggests that the thermal release of these Hg species is related to the electronegativity of the halogen, in that the Hg release temperature increases with electronegativity.

The thermal decomposition profiles for the gypsum samples were found different for both power stations A and B (Figure 2). In general, the thermal decomposition of Hg compounds in gypsum samples occurs at low temperature ranging from approximately 100 to 250 °C. The FGD-A (Figure 2a) shows multiple but convoluted peaks with a maximum at 220 °C. According to the decomposition temperatures for different Hg compounds [9], the decomposition for Hg sulphide and sulphate compounds occurs between 200-400°C, therefore Hg-S species could be the mercury compounds present in the gypsum from power station A (burning blended coals), most probably Hg sulphate compounds. However, the mean peak obtained in the gypsum samples from power station B (burning a blend of coal and pet-coke) shows a maximum at approximately 140 °C (Figure 2b). These lower temperatures correspond to decomposition for Hg halogenated

compounds [9], most probably HgCl_2 . The presence of chlorine in FGD gypsum was verified by Font et al. [21] for the same sampling campaign carried out in these two pulverized coal combustion power plants finding in fact, a higher chloride content in FGD-B than in FGD-A. Therefore, it is important to know the speciation of mercury in FGD gypsum because due to the different solubilities of Hg-S species (FGD-A) and HgCl_2 (FGD-B), a different retention could be expected in the FGD units.

The thermal decomposition profile of FGD-A presents multiple peaks (Figure 2a) suggesting that some peaks might be overlapped. With the aim to improve the resolution between successive peaks, a second and revised heating programme was utilised. The heating programme consists of three ramps during which the temperature was raised at $20^\circ\text{C min}^{-1}$ separated by isothermal intervals of 7-10 minutes. The intervals were selected in order to allow each mercury compound to be completely resolved within its characteristic desorption temperature. Figure 3 shows the thermal decomposition profile for FGD-A using the multi-ramp temperature programme. The range of decomposition temperature is the same as that in Figure 2a. However, a sharp peak is now observed at approximately 220°C confirming that Hg-S species are the main mercury compounds in this gypsum. The second peak close to 120°C suggests that HgCl_2 could be also present in FGD-A in very low concentration. X-ray Absorption Fine Structure (XAFS) studies have suggested that Hg in gypsum may be bound to Fe-containing particles in the presence of chloride [6, 22].

These results confirm the study carried out by Font et al. [21] over the partitioning of trace elements in the same two power plants. Font et al. found a higher Hg retention in FGD gypsum from power station A suggesting a major occurrence of insoluble Hg

species in the FGD facilities (Figure 2a). In the power station B it was found a higher fraction of Hg in the water streams, indicating that Hg occurs as high water soluble Hg species (Figure 2b).

According to the physical and chemical characterization of the gypsum samples carried out in this study (Table 1), no significant differences were found between a power plant burning only coal and a power plant burning a blend of coal and pet-coke. However, differences were found when the samples were analyzed by the thermal decomposition method. Therefore, this method is a useful technique to gain a better understanding of Hg behaviour in FGD facilities.

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FIGURES CAPTIONS

Figure 1. Thermal decomposition profiles of mercury halogenated compounds

Figure 2. Thermal decomposition profiles of (a) FGD-A and (b) FGD-B gypsums from A and B power station

Figure 3. Thermal decomposition profile of FGD-A gypsum using the multi-ramp temperature programme