



# Temperature programmed desorption as a tool for the identification of mercury fate in wet-desulphurization systems



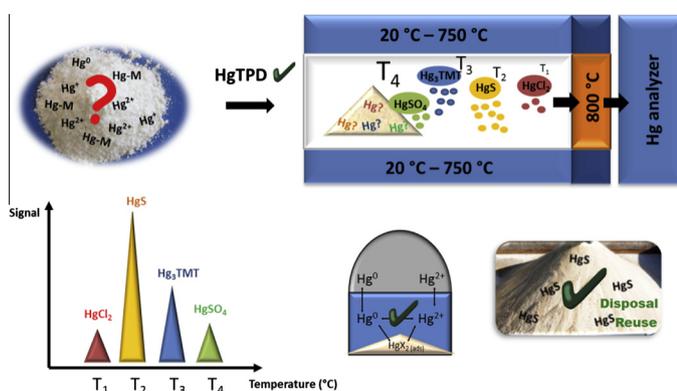
M. Rumayor, M. Díaz-Somoano\*, M.A. López-Antón, R. Ochoa-González, M.R. Martínez-Tarazona

Instituto Nacional del Carbón-CSIC, C/ Francisco Pintado Fe 26, 33011 Oviedo, Spain

## HIGHLIGHTS

- Mercury speciation in solids by thermal desorption.
- Identification of mercury species present in flue gas desulphurization gypsum.
- HgS is the preferred chemical state of mercury for long-term storage.
- Vaporisation or leaching of mercury from flue gas desulphurization gypsum can be minimised.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 15 October 2014

Received in revised form 26 January 2015

Accepted 28 January 2015

Available online 9 February 2015

### Keywords:

Mercury speciation

Wet-FGD

Gypsum

Mercury fate

HgTPD

## ABSTRACT

In this study a thermal desorption procedure (HgTPD) was used to identify mercury species in samples of gypsum obtained from wet flue gas desulphurization plants (WFGD). Gypsum from industrial coal combustion power plants and gypsum from a laboratory device that simulates mercury retention in the WFGD process were studied. It was concluded that mercury sulphide (HgS) is the mercury species present in WFGD gypsums unless an additive is used. Mercury speciation in this kind of residue can contribute to a better understanding of the reaction and adsorption behaviour of mercury species in the WFGD process and provide a deeper knowledge of the environmental impact caused by the disposal or reuse of these Hg-containing residues.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The wet flue gas desulphurization (WFGD) process is a well-established technology for air pollution control in coal-fired power plants. In this process the SO<sub>2</sub> is removed from the combustion flue gas by reaction with limestone or lime slurry. The absorbed SO<sub>2</sub> dissociates into hydrogen sulphite (HSO<sub>3</sub><sup>-</sup>) and reacts with calcium.

\* Corresponding author. Tel.: +34 985 119090; fax: +34 985 297662.

E-mail address: [mercedes@incar.csic.es](mailto:mercedes@incar.csic.es) (M. Díaz-Somoano).

The main product is calcium sulphite hemihydrate (CaSO<sub>3</sub>·1/2H<sub>2</sub>O) which, when subjected to additional oxidation with air (forced-oxidation), is converted into sulphate (SO<sub>4</sub><sup>2-</sup>) that finally crystallises as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). In the best of cases, this gypsum can be recovered as a commercial product for the wallboard or cement industry. Otherwise the gypsum is disposed of [1].

Although WFGD systems (usually referred to as scrubbers), are designed to capture sulphur species, they may also serve as sink for other pollutants, such as F, As, B, Cl, Se or Hg. These elements enter the WFGD in gaseous form or as particulate matter [2–4]. Oxidised

mercury species ( $\text{Hg}^{2+}$ ), which are soluble in water, are captured in scrubbers whose removal efficiencies range from 40 to 90% [2,5,6]. This variation in efficiency is a consequence of the wide-ranging modifications in the operational parameters and the different pollution control devices (ESP and De-NO<sub>x</sub>), employed in each plant. The main problem associated with the behaviour of mercury in WFGD systems is that once  $\text{Hg}^{2+}$  is dissolved in the scrubber slurry, it may react with other species to form  $\text{Hg}^0$  which is then re-emitted with the gases [7–10]. The problem is that Hg chemistry in WFGD systems involves several variables, some of which are difficult to control. The  $\text{Hg}^{2+}$  captured in the WFGD can be retained in the water sludge and re-circulated through the system, or it can be captured in the grained fraction of the gypsum. In the first case, mercury may accumulate throughout the slurry altering the equilibrium reactions and leading to the undesired re-emission of mercury [9,11]. In the second case, when the mercury leaves associated with the gypsum, the toxicity of this sub-product whether it is destined for future recovery or disposal needs to be controlled. However control can only be possible if the speciation and partitioning of the mercury in WFGD facilities is known in advance and if the mercury species present in the gypsum can be identified and determined.

Mercury mobility in disposal sites and mercury behaviour in gypsum utilisation processes depends on the mode of occurrence of this element. Yet, information on mercury speciation in FGD gypsum is still scarce, partly because there is no suitable analytical technique for the identification of mercury species in solids at low concentrations. Until now, sequential and selective extraction procedures [12–16] have been the conventional way to determine mercury speciation in solids but these methods are subject to certain restrictions. Apart from problems related to re-adsorption, background contamination or loss of volatile mercury, the application of selective extraction for the identification of mercury species in gypsum is limited by the solubility of the sample. The present work therefore focuses on the search for an alternative way to identify mercury species that are present in trace concentrations in gypsum from WFGD plants. One of the most promising of these methods is based on the selective thermal desorption of mercury species from the solid sample, referred to in this work as HgTPD. This method has already been employed to identify the mercury composition of soils, sediments, airborne particulate matter and FGD gypsum among others [17–21]. Nevertheless, it still needs to be validated and the scientific community has yet to demonstrate that the method is reproducible for any solid matrix.

Briefly, in this work, a thermal desorption procedure that was performed using a previously optimised and validated device [20], was employed to identify mercury species WFGD gypsum samples obtained from both industrial processes and laboratory tests under different operational conditions. The aim was to assess the scope of the method for identifying mercury species in WFGD gypsums and its capacity to predict the fate of mercury in these systems. It is expected that the knowledge obtained will allow not only a better understanding Hg–gypsum interactions, but also make it possible to predict the toxicity of this by-product when it is to be disposed of or recovered for different applications.

## 2. Experimental

### 2.1. Samples

The gypsum samples used in this work are described in Table 1. Four of them are FGD gypsum samples collected from industrial coal combustion power plants in Spain. The others were obtained using a laboratory-scale device that simulates mercury retention

in wet scrubbers [8,9,22,23]. The lab-scale experiments to produce gypsum samples were carried out at a pH in a range of 4.0–8.0.

The samples labelled A–C (Table 1) were collected from WFGD plants equipped with a wet limestone-based system under forced oxidation. All of them burned coal blends of different origin, the only exception being the plant from which gypsum B was taken. In this case, at the time of sampling, a blend of bituminous coal and petroleum coke was used as the combustible. Moreover, in this plant an additive was used in the scrubber to favour the formation of an insoluble fluorine compound [9,24]. This sample was also exceptional in that it was sampled in 2009 and stored in the laboratory until its analysis in 2014. In a preliminary study [21], it was analysed using a similar procedure.

Thirteen gypsum samples contaminated with different quantities of mercury (D–P), obtained at laboratory scale (Table 1) were also analysed. They were produced in a lab-scale reactor in different conditions. In all cases, the gypsum slurry was prepared by mixing a natural limestone or a commercial calcium carbonate with sulphuric acid. A gas stream containing  $50 \mu\text{g}/\text{m}^3$  of  $\text{Hg}^{2+}$ , generated from an evaporator (HovaCAL, IAS GmbH) was passed through the slurry solution. The first-series of slurries was prepared using different limestone samples (D–G) [23]. The second series was obtained from experiments in which different additives and ions were added (H–P) [8,9,22]. The limestone that yielded gypsum B was used in the second series.

A part of the mercury present in the inlet gas was retained in the reactor while the rest was emitted with the outlet stream. The slurry was filtered and the mercury present in the gypsum was analysed using an Advanced Mercury Analyser LECO AMA 254. The differences between the gypsum samples obtained by this procedure were a consequence of the composition of the liquor slurry. Gypsum samples D–G were produced using limestone minerals of different characteristics; gypsum H–J by adding the chemical reagents 2,4,6 trimercaptotriazine trisodium (TMT), sodium hydrosulphide (NaHS) and sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) and gypsum samples K–M by the addition of halogen ions. Gypsums N–P were obtained by adding metal ions in solution under a  $\text{CO}_2$ -enriched atmosphere.

The behaviour and distribution of the mercury in the experiments summarised above, as well as the proportion of mercury reemitted, have been described and discussed elsewhere [8,9,22,23]. In the present paper these gypsum samples were characterised for their mercury composition in order to assess the potential of the HgTPD method to confirm and improve upon previously discussed results.

### 2.2. Equipment and method

A continuous mercury analyser (RA-915) coupled to a furnace (PYRO-915), both from Lumex, were used for the mercury temperature programmed desorption (HgTPD) procedure. The analyser operates on the basis of differential Zeeman atomic absorption spectrometry and the high frequency modulation of light polarisation. The PYRO-915 furnace consists of two chambers in series, the first of which serves to pyrolyze the solid samples. In this chamber mercury compounds are released from the solid matrix in a controlled heating mode. The second chamber, kept at approximately  $800^\circ\text{C}$ , serves to reduce the mercury compounds to elemental mercury. The temperature of the first chamber is continuously monitored by means of a thermocouple. The parameters used for the selective desorption were previously optimised. The mercury compounds desorbed from the sample were carried through the chambers in a stream of air at a flow rate of  $1 \text{ l min}^{-1}$ . The heating rate from room temperature up to  $750^\circ\text{C}$  was  $50^\circ\text{C min}^{-1}$ . The mercury species were identified on the basis of the temperature at which they were released from the sample compared to the

**Table 1**  
Hg contents of the gypsum samples.

Reference	[Hg] $\mu\text{g g}^{-1}$	Observations	Reference	[Hg] $\mu\text{g g}^{-1}$	Observations
Gypsum A	1.72		Gypsum H	22.2	TMT
Gypsum B	0.23		Gypsum I	13.5	NaHS
Gypsum C	1.19		Gypsum J	14.4	$\text{Na}_2\text{S}_2\text{O}_3$
Gypsum D	21.0	From Natural limestone	Gypsum K	6.34	$\text{F}^-$
Gypsum E	0.72	From Natural limestone	Gypsum L	0.3	$\text{Cl}^-$
Gypsum F	23.1	From Natural limestone	Gypsum M	0.43	$\text{Br}^-$
Gypsum G	0.68	From commercial $\text{CaCO}_3$	Gypsum N	0.80	$\text{Fe}^{2+}$
			Gypsum O	0.94	$\text{Fe}^{3+}$
			Gypsum P	0.60	$\text{Mn}^{2+}$

**Table 2**  
Thermal dissociation temperatures corresponding to the pure mercury compounds.

Reference Hg compounds	High peak $T$ ( $^\circ\text{C}$ )	Start $T$ - End $T$ decomposition peak ( $^\circ\text{C}$ )
$\text{HgBr}_2$	$110 \pm 9$	60–220
$\text{Hg}_2\text{Cl}_2$	$119 \pm 9$	60–250
$\text{HgCl}_2$	$138 \pm 4$	90–350
HgS black	$190 \pm 11$	150–280
$\text{Hg}_3\text{TMT}$	$282 \pm 6$	100–350
HgS red	$305 \pm 12$	210–340
$\text{HgF}_2$	$234 \pm 42; 449 \pm 12$	120–350; 400–500
HgO red	$308 \pm 1; 471 \pm 5$	200–360; 370–530
HgO yellow	$284 \pm 7; 469 \pm 6$	190–380; 320–530
$\text{HgSO}_4$	$583 \pm 8$	500–600
$\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	$264 \pm 35; 280 \pm 13; 460 \pm 25$	150–370; 375–520

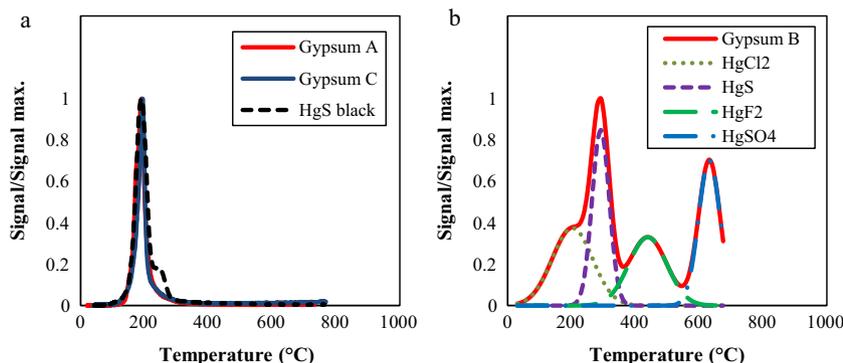
characteristic desorption temperatures of several reference mercury compounds previously recorded by the authors [20]. In addition, commercial HgS black (metacinnabar) and  $\text{Hg}_3\text{TMT}$  (mercury-TMT compound) were included in the database.  $\text{Hg}_3\text{TMT}$  was prepared according to the following procedure, 50.15 g of  $\text{HgCl}_2$  (0.075 M) was mixed with 5.01 g of  $\text{Na}_3\text{S}_3\text{C}_3\text{N}_3\text{9H}_2\text{O}$  (0.246 M). The resulting solution (pH = 6.41) was then stirred for 2 h and the white precipitated gel was dried under air flow for 24 h [25]. Table 2 summarises the maximum desorption temperatures of the Hg reference compounds used in this study i.e.,  $\text{HgBr}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgF}_2$ ,  $\text{Hg}(\text{NO}_3)_2$ , HgO, black and red HgS,  $\text{Hg}_3\text{TMT}$  and  $\text{HgSO}_4$ . These Hg reference samples were prepared by mixing each Hg pure compound with silica and then successively diluting them until a concentration of  $10 \mu\text{g g}^{-1}$  was obtained. About 100 mg of sample was used for the analysis. The mercury content of the samples, analysed by the thermal desorption device, was kept below  $10 \mu\text{g}$  to prevent the equipment from being contaminated and to avoid memory effects.

Overlapping peaks in the thermal desorption curves were deconvoluted using Origin 6.0 software. HSC Chemistry 6.1

software was used to predict the reaction mechanisms and to identify the sulphur species in the operation conditions of scrubbers.

### 3. Results and discussion

The mercury contents of the gypsum samples which range from 0.13 to  $23 \mu\text{g g}^{-1}$  are shown in Table 1. The normalised desorption profiles of the mercury species are illustrated in Figs. 1 and 2. From Fig. 1, it can be seen that the desorption profiles corresponding to the gypsum samples collected from the industrial WFGD systems (gypsums A and C) are similar, but there is an enormous difference in the case of gypsum B. The HgTDP profiles of A and C (Fig. 1a) show a simple desorption peak at  $190 \pm 11 \text{ }^\circ\text{C}$  which is the desorption temperature of the black HgS. No Black HgS is noticeable in gypsum B but there is a peak corresponding to red HgS (Fig. 1b). The difference which marks these two forms of HgS is the crystalline structure. Whereas red HgS (cinnabar) is a hexagonal crystal, black HgS (metacinnabar) is cubic. Although red HgS is more stable and common in nature than the black form, precipitation reactions at low temperature can yield metastable black HgS. HgS is usually produced by precipitation from an aqueous solution of  $\text{Hg}^{2+}$  salt with  $\text{H}_2\text{S}$  [26], but in complex waters, such as slurry liquor, the formation of HgS depends on the pH and redox potential. Previous results have shown that there is a correlation between the pH and the redox potential of the slurries [9]. Thermodynamic equilibrium data indicate that the formation of HgS is favoured in the range of pH in which the scrubbers operate (4–7.5) (Fig. 3), and although transitions between the red and black form under the conditions of gypsum disposal have not been demonstrated, the possibility that this might occur cannot be ruled out. Sample B is old WFGD gypsum taken from a power plant in 2009 and kept in the laboratory since then. This sample was analysed in the present study to compare the performance of the equipment used. It was analysed by HgTPD in a similar apparatus 5 year ago when HgS red and  $\text{HgCl}_2$  were the mercury species identified [21].



**Fig. 1.** Mercury thermal decomposition profiles of gypsum obtained at industrial scale.

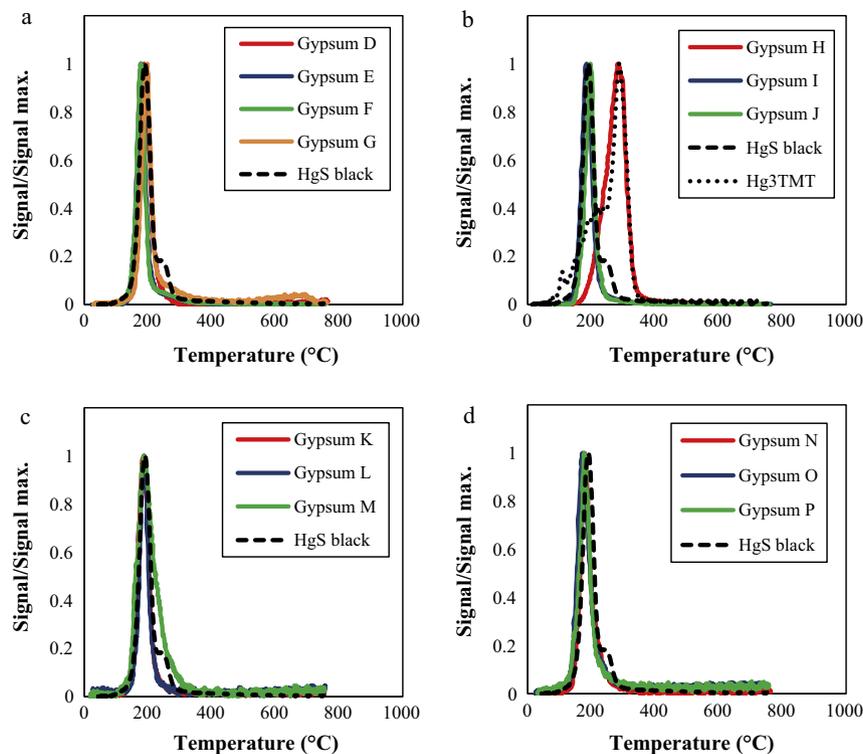
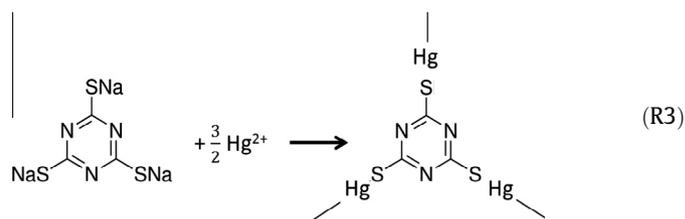


Fig. 2. Mercury thermal decomposition profiles of gypsum obtained at laboratory scale.

As mentioned above, the HgTPD profile for gypsum B (Fig. 1b), reveals a completely different mercury composition to that of A and C. Four desorption peaks at 140, 300, 440 and 625 °C, corresponding to  $\text{HgCl}_2$ , red HgS,  $\text{HgF}_2$  and  $\text{HgSO}_4$ , respectively can be identified from the deconvolution of the thermogram. The huge difference in the mercury composition of this gypsum sample shows the effects that the additive injected into the scrubber can have on mercury behaviour. The additive, in this case, aluminium sulphate, was employed to capture the fluorine present in the slurry in the form of an insoluble species in order to minimise the risk of fluoride leaching when the gypsum was finally disposed of. The identification of  $\text{HgCl}_2$ , red HgS,  $\text{HgF}_2$  and  $\text{HgSO}_4$  in the gypsum confirms that this additive modifies the equilibrium reactions in the scrubber [4,24,27]. During the precipitation of the gypsum a part of the mercury contributes to the formation of the  $\text{HgF}_2$  and the  $\text{HgCl}_2$  species that are adsorbed onto the gypsum particles. It might be expected that at the pH of the scrubber liquor [4–7], the  $\text{HgCl}_2$  would solubilise. However, as already demonstrated [11], in this particular plant the aqueous phase of the gypsum B slurry shows a higher concentration of Cl ( $3420 \mu\text{g g}^{-1}$ ) and there is a high concentration of  $\text{HgCl}_2$  in the aqueous phase of this slurry which favours adsorption onto the solid. In any case discussion as to how the additive modifies mercury behaviour in the scrubber lies outside the scope of this work. Here it is pointed out that the HgTPD method is a useful tool for understanding these mechanisms, as it is able to differentiate between the mercury species formed under different conditions.

From the HgTPD analysis, it can be inferred that mercury speciation in the synthetic gypsum samples does not depend on the characteristics of the limestone. The desorption profiles obtained from the gypsum samples produced in the lab-scale device using different limestone (Gypsum D–G) show a maximum desorption peak at around  $190 \pm 11$  °C, that corresponds to the desorption temperature of black HgS, which favours its adsorption onto the gypsum.

As mentioned in the first section of this study, the possibility of using additives to minimise the re-emission of mercury from the WFGD is the subject of extensive study [8]. To understand the effect of the most common of these additives (TMT, NaHS and  $\text{Na}_2\text{S}_2\text{O}_3$ ), the mode of occurrence of mercury in the gypsum samples produced (Gypsum H–J), was also investigated. The HgTPD desorption profiles (Fig. 2b) show the maximum desorption temperature of black HgS ( $190 \pm 11$  °C), for most of these additives. The HgS compound was produced in the slurry when NaHS and  $\text{Na}_2\text{S}_2\text{O}_3$  were used according reactions (R1) and (R2). The HgS was then adsorbed onto the gypsum particles [8]. Only when the TMT additive was employed, a shift in the thermogram was observed. In this sample, the compound  $\text{Hg}_3\text{TMT}$ , which was desorbed at  $282 \pm 6$ , was formed via reaction (R3).



As can be seen in Fig. 2, the desorption profiles obtained for the gypsum samples produced in the presence of halides ( $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ ) in the scrubber solution (Gypsum K–M) are all similar. The main desorption peak again occurs at  $190 \pm 11$  °C (Fig. 2c). Halides can form different complexes with mercury in solution, but these compounds are soluble in water and only insoluble HgS was identified in the gypsum.

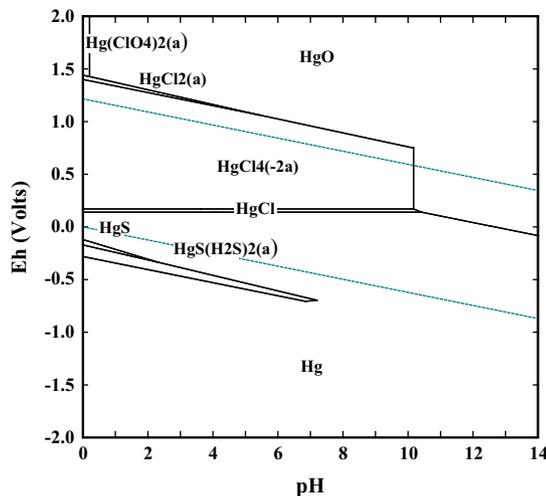


Fig. 3. Eh–pH diagram for sulphur species at 40 °C (1 mM S).

Similar results were obtained when metallic ions ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ ) were added to the scrubber solution (Gypsum N–P), confirming that, in most conditions, black HgS is the species present in the WFGD gypsum (Fig. 2d). Previous studies by the authors [8] have indicated the presence of metal ions in the scrubber liquor as participants of mercury reduction and re-emission. However, identification of mercury species by HgTPD in the gypsum obtained in the presence of metals in the slurry shows that these metallic ions do not modify the fate of mercury HgS which is again the main species associated with gypsum. As might be expected the amount of mercury captured when the reduced form of the metal is present in the scrubber is lower than when the metallic ion is in an oxidised form (Table 1).

These results confirm that oxidised mercury in gas phase, which is absorbed in the scrubber liquor, undergoes a series of reactions. These reactions, some of which have been observed previously [8,9,23,27], are summarised in Fig. 4. According to the HgTPD results, the formation of solid HgS in the gypsum by-products is beyond doubt. Since the different reactions depend on the composition, pH and redox potential of the slurry, the concentration of mercury that finally forms HgS must be a function of the slurry's composition. The presence of metallic ions originating from limestone impurities [23] or from the use of additives to the scrubber solution for enhancing mercury capture modifies mercury partitioning between the solid and liquid phase of the scrubber solution

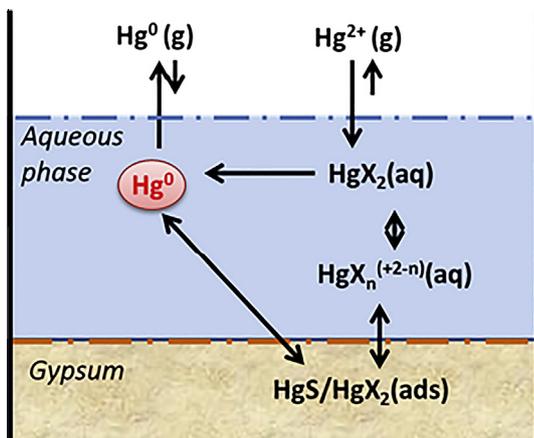


Fig. 4. Hg–gypsum interactions [8,9,20,24].

[8]. Although theoretically, complexed mercury in solution can be partially adsorbed onto the gypsum particles, species other than HgS were only identified in those cases where additives were added, that is, when the composition of the liquor was synthetically modified.

Because the main species from the interaction of the mercury with gypsum in WFGD is HgS, which is insoluble in water, leaching is not likely to occur when the gypsum is disposed of. If the gypsum is to be reused, wallboard production will be its main application. The WFGD–gypsum is then dried before it is transported to wallboard manufacturing plants to facilitate its handling. The maximum temperatures in this step range between 77 °C and 110 °C, which means that evaporation of the HgS is not expected. In the calcination step, the temperature has to be increased to above 130 °C to promote the release of 1–½ molecules of hydration water, but kept below 180 °C to avoid the formation of anhydrous calcium sulphate. Some mercury might be lost during the calcination step [28,29] even though the temperatures reached in this step (130–180 °C), are lower than the maximum temperatures of decomposition of black and red HgS (190 ± 11 and 305 °C ± 12 respectively). It should be noted that HgS is the preferred chemical state of mercury for long-term storage, because these species has better leaching properties and a lower vapour pressure than the other compounds. In addition it is a chemically stable species which provides an additional barrier to leaching. Thus, by using an appropriate stabilization method and suitable additives, the possibility of the vaporisation or leaching of mercury from FGD–gypsum into the environment can be minimised or even eliminated altogether.

From the results obtained in this work, it can be concluded that the HgTPD method proposed is a valuable tool for identifying mercury species in gypsum samples obtained in WFGD plants in different conditions. In particular, the results obtained from the analysis of the different gypsum samples produced at industrial and lab-scale conditions in different slurry compositions, contribute to a better understanding of the reaction and adsorption behaviour of mercury species in a wet scrubber. Moreover the speciation of mercury in WFGD gypsum makes it possible to predict the behaviour of these mercury species when the solid is disposed of or reused.

## Acknowledgments

The financial support for this work was provided by the project CTM2011-22921. The authors thank the Spanish Research Council (CSIC) for awarding Ms. Marta Rumayor a JAE–predoc fellowship.

## References

- [1] Kil S, Hansen BB. Multi-scale experiments and simulation tools for optimisation of wet flue gas desulphurisation plants. *VGB Power Tech* 2011;3:89–93.
- [2] Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, et al. Status review of mercury control options for coal-fired power plants. *Fuel Process Technol* 2003;82(2–3):89–165.
- [3] Zhong LP, Cao Y, Li WP, Xie K. Effect of the existing air pollutant control devices on mercury emission in coal-fired power plants. *J Fuel Chem Technol* 2010;38(6):641–6.
- [4] Álvarez-Ayuso E, Querol X, Tomás A. Environmental impact of coal combustion desulphurisation plant: abatement capacity of desulphurisation process and environmental characterisation of combustion by-products. *Chemosphere* 2006;665:2009–17.
- [5] Cheng CM, Hack P, Chu P, Chang YN, Lin TY, Ko CS, et al. Partitioning of mercury, arsenic, selenium, boron, and chloride in a full-scale coal combustion process equipped with selective catalytic reduction, electrostatic precipitation, and flue gas desulfurization systems. *Energy Fuels* 2009;23:4805–16.
- [6] Meij R, te Winkel H. The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations. *Atmos Environ* 2007;41:9262–72.

- [7] Lu R, Hou J, Xu J, Tang T, Xu X. Effect of additives on  $\text{Hg}^{2+}$  reduction and precipitation inhibited by sodium dithiocarbamate in simulated flue gas desulfurization solutions. *J Hazard Mater* 2011;196:160–5.
- [8] Ochoa-González R, Díaz-Somoano M, Martínez-Tarazona MR. Control of  $\text{Hg}^0$  re-emission from gypsum slurries by means of additives in typical wet scrubber conditions. *Fuel* 2013;105:112–8.
- [9] Ochoa-González R, Díaz-Somoano M, Martínez-Tarazona MR. The capture of oxidized mercury from simulated desulphurization aqueous solutions. *J Environ Manage* 2013;120:55–60.
- [10] Heidel B, Hilber M, Scheffknecht G. Impact of additives for enhanced sulfur dioxide removal on re-emissions of mercury in wet flue gas desulfurization. *Appl Energy* 2014;114:485–91.
- [11] Córdoba P, Font O, Izquierdo M, Querol X, Tobías A, López-Antón MA, et al. Enrichment of inorganic trace pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants. *Fuel Process Technol* 2011;92:1764–75.
- [12] Bloom NS, Preus E, Katon J, Hiltner M. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal Chim Acta* 2003;479(2):233–48.
- [13] Reis AT, Rodrigues SM, Davidson CM, Pereira E, Duarte AC. Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere* 2010;81(11):1369–77.
- [14] Biester H, Scholz C. Determination of mercury binding forms in contaminated soils: mercury pyrolysis versus sequential extractions. *Environ Sci Technol* 1997;31:233–9.
- [15] Fernández-Martínez R, Rucandio I. Assessment of a sequential extraction method to evaluate mercury mobility and geochemistry in solid environmental samples. *Ecotoxicol Environ Saf* 2013;97:196–203.
- [16] Pinedo-Hernández J, Marrugo-Negrete J, Díez S. Speciation and bioavailability of mercury in sediments impacted by gold mining in Colombia. *Chemosphere* 2015;119:1289–95.
- [17] Reis AT, Coelho JP, Rucandio I, Davidson CM, Duarte AC, Pereira E. Thermo-desorption: a valid tool for mercury speciation in soils and sediments? *Geoderma* 2015;237–238:98–104.
- [18] Shuvaeva OV, Gustaytis MA, Anoshin GN. Mercury speciation in environmental solid samples using thermal release technique with atomic absorption detection. *Anal Chim Acta* 2008;621:148–54.
- [19] Reis AT, Coelho JP, Rodrigues SM, Rocha R, Davidson CM, Duarte AC, et al. Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. *Talanta* 2012;99:363–8.
- [20] Rumayor M, Díaz-Somoano M, Lopez-Anton MA, Martínez-Tarazona MR. Mercury compounds characterization by thermal desorption. *Talanta* 2013;114:318–22.
- [21] Rallo M, Lopez-Anton MA, Perry R, Maroto-Valer MM. Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition. *Fuel* 2010;89:2157–9.
- [22] Ochoa González R, Díaz-Somoano M, López Antón MA, Martínez-Tarazona MR. Effect of anion concentrations on  $\text{Hg}^{2+}$  reduction from simulated desulphurization aqueous solutions. *Chem Eng J* 2013;214:165–71.
- [23] Ochoa-González R, Díaz-Somoano M, Martínez-Tarazona MR. Influence of limestone characteristics on mercury re-emission in WFGD systems. *Environ Sci Technol* 2013;47:2974–81.
- [24] Álvarez-Ayuso E, Querol X, Ballesteros JC, Giménez A. Risk minimisation of FGD gypsum leachates by incorporation of aluminium sulphate. *Sci Total Environ* 2008;406:69–75.
- [25] Henke KR, Robertson D, Krepps MK, Atwood DA. Chemistry and stability of precipitates from aqueous solutions of 2,4,6-trimercaptotriazine, trisodium salt, nonahydrate (TMT-55) and mercury (II) chloride. *Wat Res* 2000;34:3005–13.
- [26] Patnaik P. *Handbook of inorganic chemicals*. p. 579.
- [27] Ochoa González R, Díaz-Somoano M, López Antón MA, Martínez-Tarazona MR. Effect of adding aluminum salts to wet FGD systems upon the stabilization of mercury. *Fuel* 2012;96:568–71.
- [28] Heebink LV, Hassett DJ. FGD gypsum processing. In: 2003 International ash utilization symposium. Center for Applied Energy Research, University of Kentucky, paper #75.
- [29] Leiva C, García Arenas C, Vilches LF, Vale A, Gimenez A, Ballesteros JC, et al. Use of FGD gypsum in fire resistant panels. *Waste Manage* 2010;30:1123–9.