Review

Behaviour of antimony during thermal treatment of Sb-rich halogenated waste

J. Klein[a], S. Dorge[a,*], G. Trouvé[a], D. Venditti[b], S. Durécu[b]

[a] Laboratoire Gestion des Risques et Environnement, 25 rue de Chemnitz, 68200 Mulhouse, France
[b] TREDI Département de Recherche, Technopôle de Nancy-Brabois, 9 avenue de la Forêt de Haye, BP 184, 54505 Vandœuvre-lès-Nancy, France

ARTICLE INFO

ABSTRACT

Antimony compounds have a wide range of industrial applications, particularly as additives in flame retardants. To ensure environmentally friendly waste incineration of Sb-rich wastes, it is essential to strengthen the knowledge about the fate of antimony and the potential formation of harmful species. Investigations should be conducted particularly in relation with the main operational parameters controlling the process, chiefly temperature, residence time and air supply in the oven and in the *post*-combustion zone, prior final adapted cleaning of the flue-gas stream. Experimental studies focusing on antimony behaviour were undertaken through laboratory-scale thermal treatment at 850 °C and 1100 °C of a Sb-rich halogenated waste, originating from the sector of flame retardants formulation. The configuration of our laboratory experimental device allowed to achieve only low oxidative conditions in the waste bed, but high oxidative strength coupled with high temperature and sufficient gas residence time in the *post*-combustion zone, as prescribed during the incineration of hazardous wastes. Atomic absorption spectroscopy was used to assess the partition of antimony in the different compartments of the process. The oxidation degree of antimony in the gas-phase was determined by the use of electrochemical techniques, namely polarography coupled with anodic stripping voltamperometry. The partition of antimony between the residual ash and the gas-phase under moderate oxidative conditions in the waste bed was constant, whatever the temperature: the volatilization rate for antimony was ~64%, while a ~36% fraction remained in the residual bottom ashes. But interestingly, while at 850 °C, antimony was mainly present in the gas-phase at a +III oxidation degree, an increase in temperature of 250 °C favoured the presence of antimony to its highest oxidation degree +V in the flue-gas stream, a valence known to be involved in less toxic species.

© 2008 Elsevier B.V. All rights reserved.

Contents

* Corresponding author. Tel.: +33 3 89 32 76 55; fax: +33 3 89 32 76 61.
  E-mail address: sophie.dorge@uha.fr (S. Dorge).

1. Introduction

For decades antimony (Sb) and its compounds have been widely used in various industrial sectors, especially as additives in the manufacture of flame-retardants, accounting for about 90% of global antimony trioxide consumption. A method to induce flame retardance was indeed to introduce a halogen-containing organic compound combined with Sb_2O_3, generally on a 5:1 stoichiometric ratio of halogen to antimony [1–3]. Sb_2O_3 by itself is not a flame retardant, and halogenated organic compounds (mainly bromine and chlorine) alone show only a weak flame retardant effect. But when combined under thermal oxidative treatment, these compounds act synergistically, 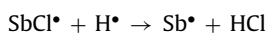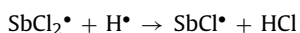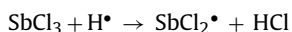through a complex radical mechanism to interrupt the exothermic processes and inhibit combustion [3,4]. Br compounds are much more flame retardant than Cl compounds.

Below 300 °C through thermal decomposition, the halogen first forms hydrogen halides (HX), that probably react in the solid phase through oxidative conditions with Sb_2O_3, to form volatile antimony trihalides (SbX_3) or oxyhalides. In such oxidative conditions, Sb_2O_3 is thus supposed to act as a halogen shuttle bringing antimony trihalides (SbX_3) or oxyhalides in the vapor phase [3–5].

$$Sb_2O_3 + 6HX \rightarrow 2SbX_3 + 3H_2O$$
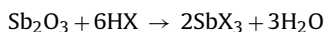
These volatile compounds then act as scavengers in the gaseous phase, sequestrering the high energy reactive free radicals ($O^\bullet$, $H^\bullet$ and $^\bullet OH$) which are required to propagate the flame [4,5].

The antimony trihalogenated interferes more strongly with the energetic radicals than the hydrogen halide, probably due to the trivalent state of antimony:

$$SbCl_3 + H^\bullet \rightarrow SbCl_2{}^\bullet + HCl$$

$$SbCl_2{}^\bullet + H^\bullet \rightarrow SbCl^\bullet + HCl$$

$$SbCl^\bullet + H^\bullet \rightarrow Sb^\bullet + HCl$$

Parallel oxidation reactions may also occur, during which antimony oxides and $Sb^\bullet$ radicals participate to the inhibition reaction of the hot radicals. The whole process is therefore deprived of oxygen, generating products from incomplete combustion and an increase in smoke density.

The behaviour of antimony and the thermal decomposition mechanism of Sb-rich halogenated compounds under reducing conditions is not completely understood, but it was reported that under pyrolysis, Sb_2O_3 synergist did not react with brominated compounds in vacuum in the first step (~400 °C), but evaporated as the dimer Sb_4O_6 [6], a bicyclic cage structure of Sb_2O_3 (Sb+III). Depending on the kind of flame retardant and on the waste matrix composition, partial debromination occurred in a separate step at higher temperature, along with the cleavage of polymer chains. In presence of Sb_2O_3, such debromination reactions based on the thermal scission of macromolecules were more pronounced, leading also to $SbBr_3$ formation. Sb_4O_6 is known to sublimate in vacuum at $T > 400$ °C, while under thermal oxidative conditions it does not vaporize at low temperatures (boiling point 1425 °C) [7].

The thermal degradation behaviour of flame retardants is of interest, since such compounds may be disposed-off in waste incinerators, and also involved in accidental fires. Nowadays zinc borates emerge for the replacement of antimony oxides as synergists for halogenated fire retardant additives [8], but many end-of-life residues still contain Sb-rich halogenated flame-retardants (e.g. plastics, polymer-based materials, *e*-wastes, *etc.*. . .). Antimony is often present as a trace element, contributing to less than 0.2% of the total weight, but concentrations can rise to several percents in flame-retardants formulations as well as in some manufactured products, like PVC, containing generally 1–10% Sb by weight [3].

In a strictly controlled oxidative thermal process like incineration, antimony may be found either in the bottom ash or in various air pollution control residues (APC), or even condensed in cold points of the equipment, depending on the composition of the waste, the geometry of the combustor and the operating conditions (temperature, air supply, *etc.*. . .). Under strictly controlled oxidative conditions, the volatility of antimony is indeed enhanced when increasing Cl (or Br) levels, based on both theoretical considerations and experimental tests [7,9]. A part of Sb thus volatilizes, and subsequently rapidly condenses, mainly on submicronic particulate matter [10]. These particles can be scrubbed and captured downstream if an effective particle removal and full-gas cleaning system are present, and Sb finally concentrates in the various APC (fly ashes, lime, activated carbon. . .). Based on the incinerator geometry, such fine condensed particles may also be distributed on various cold points of the equipment.

During uncontrolled thermal processings like open-burning without temperature and air supply control and without complete final flue-gas cleaning, environmental impacts are of concerns, over the potential emission of noxious compounds in the atmosphere. Under low thermal oxidative strength, Sb_2O_3 is indeed a very volatile compound, its volatilization starting at about 600 °C [9]. Congruently, when a waste containing brominated flame retardant was processed in reducing conditions, it was shown that Sb_2O_3 synergist did not react with halogenated compounds in vacuum in the early step, but it first evaporated as Sb_4O_6 [6].

The aim of our study was to simulate, at a laboratory scale, the thermal treatment of a Sb-rich halogenated waste originating from the manufacture of flame retardants, in order:

(i) to determine in which proportion the antimony volatilizes under moderate oxidative conditions in the waste bed, and to test and implement an effective Sb-trapping system for flue-gas cleaning,

(ii) to investigate the subsequent fate and behaviour of Sb in the flue-gas stream under strict oxidative *post*-combustion conditions, at both 850 °C and 1100 °C, corresponding to two different realistic waste-incineration scenari. The first temperature (850 °C) corresponds to the *post*-combustion temperature prescribed during the incineration of non-halogenated hazardous wastes [11], but also of non-hazardous wastes, like household wastes [12], as encountered in a common household waste incinerator. The highest temperature chosen in this study (1100 °C), is the *post*-combustion temperature applied during full-scale incineration of highly halogenated hazardous is specialized plants. The French regulation related to the incineration and co-incineration of hazardous wastes [11], in full-compliance with the European Waste Incineration Directive [13], indeed states that, if the waste contains more than 1% of halogenated organic substances, expressed as chlorine, the temperature of the gases resulting from the incineration process has to be raised to 1100 °C for at least 2 s.

The study of the oxidation degree of antimony contained in the flue-gas has been performed by implementing a gas-scrubbing system downstream the furnace, allowing to approach the chemical species present in the exhaust gas, but not speciation *sensu stricto, i.e.* the determination of the exact chemical form in which Sb is involved in association with other elements such as O, Cl, H, Br, *etc.* [14]. The knowledge of the speciation, but also of the sole degree of oxidation of antimony, (+V, +III, 0, or −III) is of great concern to investigate health and environmental impacts of the thermal treatment process.

The toxicity of Sb indeed depends greatly on its oxidation state. Antimony at the valence +III is well known to be involved in the most toxic species, like SbH_3, Sb_2O_3 or $SbCl_3$, whereas the pentavalent form is considered to be about 10 times less toxic [15]. Antimony compounds have been associated with dermatitis and irritation of respiratory tract, as well as interfering with normal function of the immune system. In contrast to As, there is evidence that Sb is not detoxified *via* methylation in mammals [15]. The genotoxicity and carcinogenicity of antimony compounds have been reviewed recently [16], confirming previous findings. The International Agency for Research on Cancer (IARC) has reported that there is sufficient evidence for the carcinogenicity of antimony trioxide in experimental animals [17]. Acute antimony intoxication may cause nausea, sore throat, diarrhoea, vomiting, stiffness, blood infection, and inflammation of eyes, skin, upper respiratory tract or alimentary canal. In some cases, liver lesion, pneumonia or arrhythmia may also be observed [15].

The study presented herein is based on antimony mass balance experiments, performed through the determination of total Sb in the exhaust gas by atomic absorption spectrometry and the analysis of its oxidation degree by polarography coupled with anodic stripping voltamperometry. These assessments were first conducted after the treatment of pure antimony mineral species (Sb_2O_3, Sb_2O_5, $SbCl_3$) in order to test the oxidative strength in our laboratory furnace, and to check the efficiency of the whole Sb-trapping system in our experimental apparatus. These experiments were useful to find proper trapping solutions. They also allowed the comparison with thermodynamic behaviour (vapor pressures, boiling point, compositions at equilibrium). Thermal treatment of an industrial Sb-rich halogenated residue, classified as an hazardous halogenated waste, was then performed by applying two different temperatures (850 °C and 1100 °C) and high oxidative conditions in the *post*-combustion zone, according to prescribed conditions in municipal waste incinerators [12] and specialized hazardous waste incineration facilities [11], respectively.

2. Materials and methods

2.1. Presentation of the samples

The study of the behaviour of antimony through thermal treatment was first conducted with pure single mineral species: antimony trioxide (Aldrich, 99.9%), antimony pentoxide (Aldrich, 99.995%) and antimony trichloride (Fluka, ≥99%). In a second experiment, the thermal treatment of the Sb-rich halogenated waste was conducted. This waste was a non-homogeneous paste, containing 30.9% water. Antimony was present in the formulation under the form of Sb_2O_3. CHNS elemental analysis resulted in 17.9% C, 3% H, 1.6% N and 0.4% S. The elementary analysis with X-ray fluorescence detection showed an antimony content of 1.46%, and an overall mass content of halogenated compounds, expressed as total chlorine, of 4.59% (9.09% bromine and 0.55% chlorine). These halogens were mainly present under the form of organic compounds that could easily be converted into halides by combustion, as shown based on the French standardized method NF EN 14582 [18]. Further other

metallic elements were present in smaller amounts in the waste, such as titanium (1%), zinc (0.3%) or aluminium (0.3%). The mass content of alkaline earth elements was very low, near 1%.

2.2. Experimental devices for thermal treatment and exhaust-gas scrubbing

The experimental thermal treatment device was a 4.5 cm wide and 130 cm in length tubular quartz reactor, heated by a horizontal furnace-tube obtained from Lenton Thermal Design. The whole system is illustrated in Fig. 1. An air flow of 125 NL h^{-1} was injected in the reactor to ensure high oxidative conditions and a residence time of the gases in the isotherm *post*-combustion area of the furnace of at least 2 s, in full compliance with current French and European regulations related to waste incineration. The reactor was equipped with a removable ceramic nacelle allowing the introduction of the samples. This experimental device constitutes a licked bed in which the air flows on the top of the nacelle, instead of flowing across it. It was reported that the batch regimes in such a device led to form a local reductive atmosphere in the waste bed [19]. A gas-scrubbing system was placed downstream the reactor, as depicted in Fig. 2, consisting of serial flasks in which the gas was brought in intensive contact with a scrubbing liquid. This configuration in series allowed to check that all the volatilized antimony species were trapped in the scrubbing solutions. Three types of gas–liquid contacting systems were used, the first flask remaining empty for guard. Vessels nos. 2, 3 and 4 were equipped with a nozzle allowing to bubble gas through liquid, while in flasks nos. 5 and 6 a porous frit was used to disperse the gas. The main difference between these two types of gas–liquid contactors is the contact surface available for exchanges between gas and liquid phases. The porous frits created optimal larger contact surfaces in flasks nos. 5 and 6, but they were sometimes plugged by soot particles, confirming the possibility of a local reductive atmosphere in the waste licked bed. Flasks nos. 2–4 were thus placed upstream to trap such soot particles and prevent any damage to porous nozzles in vessels nos. 5 and 6. The role of the ultimate contactor (no. 6) was to validate the efficiency of the whole trapping device. As recommended by the French standardized method NF EN 14385 [20], the Sb-mass recovered in this final vessel should not exceed 10% of the mass trapped in the penultimate flask (no. 5).

To quantify the antimony emitted during the thermal treatment of the studied residues, the scrubbing solution used in the gas–liquid contactors contained 5 mol HCl/L [21]. Another scrubbing solution, containing 1.5% H_2O_2 and 3.3% HNO_3 (w/w), was recommended by the French standardized procedure NF EN 14385 [20] focusing on the monitoring of metals and metalloids in gas emissions from fixed sources, like incineration plant stacks. Such an oxidizing acid solution was not appropriate in the present study, because it strongly influenced the speciation of the scrubbed antimony and did not trap any antimony species.

An air pump was placed at the output of the last gas–liquid scrubber, ensuring a sufficient suction of the air flow, relative to the insufflated air. The whole system was depressurized, allowing the minimizing of leakages. After the introduction of the nacelle containing the sample in the isothermal zone, the process was carried out for half an hour and it was considered over 15 min after the fume dissipation in the gas-trapping system, allowing the withdrawal of the nacelle. Each experiment was performed three times. Such a residence time in the furnace did not model full-scale thermal treatment, since a waste is generally processed within few hours under thermal constraint in a waste treatment plant, but it was sufficient to ensure a high degree of thermal decomposition of the introduced sample.

To recover and quantify the whole amount of antimony deposited on the reactor walls during each thermal treatment test,
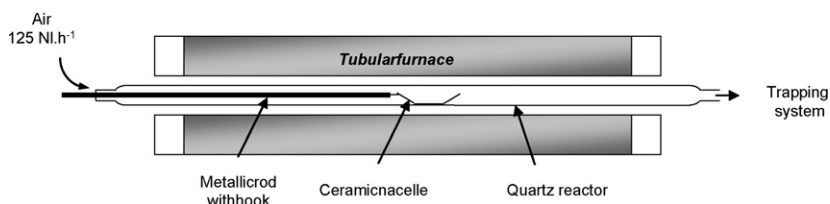
Fig. 1. Experimental thermal treatment device.

a rigorous washing method of the reactor was developed. It consisted in a rinsing of the cooled reactor by a 5 mol HCl/L solution, which was subsequently analyzed by Flame Atomic Absorption Spectroscopy to determine the amount of Sb deposited on the reactor walls. The reactor was then rinsed by water and rubbed with an adapted brush. The last cleaning test consisted in soaking the reactor in 10% HNO_3 (w/w) solution during 24 h.

2.3. Antimony analyses

2.3.1. Microwave-assisted digestion of solid samples

Solid materials (the raw waste and the ashes resulting from the thermal treatment processes) were completely digested with a hot mixture of hydrochloric, nitric and hydrofluoric acid [22,23], by adding 6 mL of HCl, 2 mL of HNO_3 and 1 mL of HF to 0.7 g of solid in a Teflon bomb, and heating to 180 °C in a microwave oven by applying the following heating program: 10 min at 120 °C, 30 min at 180 °C, 1 h cooling. A further thermal cycle was performed at 200 °C after neutralization with 2 g of orthoboric acid.

2.3.2. Analysis of total antimony concentrations in liquids

Total antimony concentrations were determined in liquids (the scrubbing solutions from the gas–liquid contactors, the solutions resulting from the washing of the reactor and the liquids obtained from the digestion of solids) by Flame Atomic Absorption Spectroscopy (AA 20 BQ+ from VARIAN), after addition of an antimony internal standard (stock solution: 1000 mg Sb_2O_3/L in 5 mol HCl/L, Fluka). Antimony concentrations in analytical blanks and standard solutions were regularly controlled. The wavelength used for the analysis of antimony was 231.2 nm. Under this configuration, the limit of quantification of the AA 20 BQ, was 1.5 mg/L of antimony. The standard relative deviation for the measurement of the metalloid concentration by FAAS was lower than 2%. Antimony partitioning is expressed in mass percent in bottom ashes and exhaust gas with a relative standard deviation of 10%.

2.3.3. Determination of Sb(III) and Sb(V) concentrations in liquids

Polarography and anodic stripping voltamperometry were used to determine Sb(III) and Sb(V) concentrations in liquids. Such methods have proven useful to distinguish the different oxidation degrees of antimony in various concentrations of supporting electrolyte, by using a hanging mercury drop electrode (HMDE). According to Bond et al. [24], in an electrolyte containing 0.1 mol HCl/L, Sb(III) solely can be reduced to Sb(0) at a HMDE to form an antimony amalgam Sb(Hg), while in a 5 mol HCl/L solution, both Sb(III) and Sb(V) forms can be reduced. By deducing the electrochemical signals obtained with both electrolytes, the concentration of Sb(V) can be calculated. The polarograph POL 150 from CTB CHOFFEL was used for the anodic pulse voltamperometric analyses. The electrolytes were prepared by dilution of a concentrated hydrochloric stock solution (12 mol HCl/L, Prolabo), and the antimony standard solution was the one used also for the Flame Atomic Absorption Spectroscopy determinations. The following parameters were applied: deposition time 200 s and response time 30 s for anodic re-dissolution, pulse amplitude of 25 mV, and pulse time 40 ms for stripping voltametry. The limit of quantification of the apparatus used in anodic stripping voltamperometry was 0.03 mg per liter of antimony. The standard relative deviation for the measurement of the metalloid concentration by polarography was lower than 2%.

2.4. Thermogravimetric analyses (TGA)

Experiments were conducted with a SETARAM SETSYS thermobalance which was operated with a vertical gas flow of air of 5 NL h^{-1}. The tests were conducted with pure antimony oxides and with the Sb-rich halogenated waste at operating temperatures ranging from 20 °C to 1100 °C with a heating temperature rate of 5 °C min^{-1}. TGA were also performed at an isothermal temperature of 1100 °C during 6 h under an air flow of 10 NL h^{-1}.

2.5. XRD measurements

The XRD measurements were performed with a diffractometer PANalytical (type X'pert PRO) with a X'celerator linear position detector equipped with a monochromator. All the measurements were realized using Cu Kα1 radiation. For the analysis, the sample was deposited on a low-adsorbent silicon support with a rotation rate equal to one turn per second. For the identification of the crystallographic phases, the International Centre for Diffraction Data
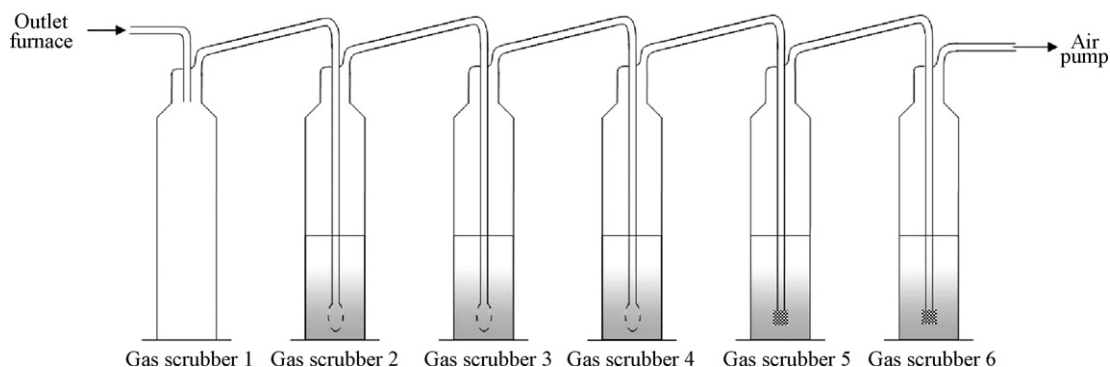

Fig. 2. Experimental gas–liquid contacting devices.

(ICDD) data files were preferentially used with the X'pert HighScore (version 2.2a) and X'pert Data Collector (version 2.0) softwares. The XRD measurements were performed on the bottom ashes obtained from the thermal treatment of pure Sb_2O_3 at 850 °C and of the halogenated waste at 1100 °C.

2.6. TEM observations

All TEM observations were performed with a Philips CM20 microscope with a LaB6 cathode operating at 200 kV. Elemental analysis was carried out by Energy Dispersive X-ray Spectrometry (EDXS) with an EDAX spectrometer. Samples were suspended in anhydrous ethanol through 2–3 min sonication to obtain a dilute and homogeneous suspension. A drop of the sonicated suspension was deposited onto a carbon film supported on a copper grid and then introduced into the microscope column. The TEM characterizations were performed on the bottom ashes obtained from the thermal treatment of pure Sb_2O_3 at 850 °C and of the halogenated waste at 1100 °C.

3. Results and discussion

3.1. Thermal treatment of single mineral species

Fig. 3 shows the proportion of antimony which was volatilized during the thermal treatment of pure compounds (Sb_2O_3, Sb_2O_5 and $SbCl_3$) at 850 °C, compared with the residual antimony found in the bottom ashes. Partitioning of volatile antimony deposited on the reactor walls and trapped in the wet scrubbers is also detailed. In our laboratory furnace at 850 °C, the antimony contained in Sb_2O_3 volatilized at 62%, with a partitioning between walls of the reactor and the scrubbers of 3% and 59%, respectively, while a proportion of 38% of the element remained in the bottom ash. In the case of antimony pentoxide, no volatilization of Sb was observed at 850 °C, the whole amount of introduced Sb_2O_5 remained in the nacelle after the thermal treatment trial, confirming also that in our experimental device no significant quantity of fine powered material was swept into the transport gas.

Thermogravimetric experiments performed in parallel under oxidative conditions are presented in Fig. 4a. Drastic weight losses from both pure Sb_2O_3 and Sb_2O_5 under air flow were achieved only beyond 900 °C, indicating thermal stability below such temperature. For Sb_2O_3, a slight mass loss (6%) was observed at 400 °C, followed by a small mass increase of 1% between 544 °C and 553 °C, corresponding to the partial oxidation of Sb_2O_3 under the form of the thermally more stable Sb_2O_4, a double molecule with mixed valence containing Sb in the oxidation states +III and +V, as already
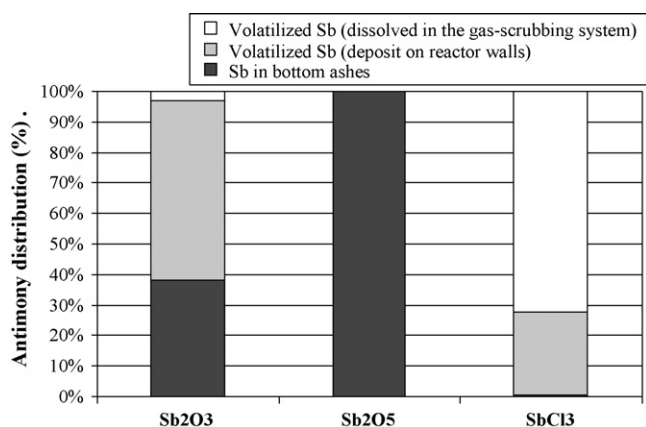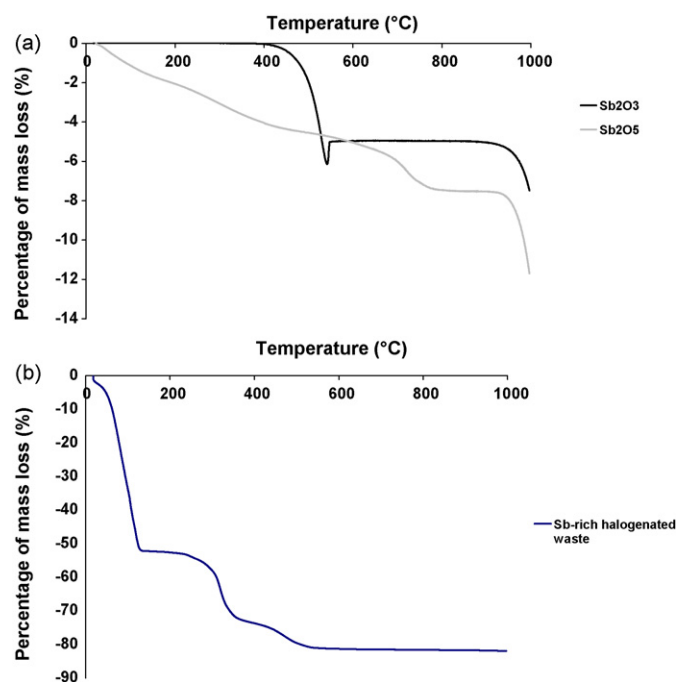

Fig. 4. (a) Thermograms of pure antimony oxides at 5 °C min^{-1} under air at 5 NL h^{-1} (b) Thermogram of the Sb-rich halogenated waste at 5 °C min^{-1} under air at 5 NL h^{-1}.

evidenced by previous studies [9,25]. The formation of this diantimonytetraoxide was confirmed by our XRD measurements and TEM/EDXS observations performed on the bottom ashes obtained after the thermal treatment at 850 °C of pure Sb_2O_3. The XRD measurements showed the existence of the orthorhombic antimony oxide α-Sb_2O_4. Fig. 5 shows the bright field TEM micrograph of the bottom ashes. In agreement with the XRD data, only Sb_2O_4 particles were present (Fig. 5). Indeed, the related SAED pattern insert of Fig. 5 displayed in the [3 $\bar{1}$ 2] zone axis diffraction spots characteristic of the orthorhombic structure of the cervantite α-Sb_2O_4 (space group: Pna2$_1$). The EDXS analysis confirmed the presence of antimony and oxygen with an atomic ratio Sb/O close to the theoretical atomic ratio Sb/O corresponding to Sb_2O_4 and equal to 0.33. A residence time of at least 6 h at 1100 °C was necessary to achieve 90% of mass loss by volatilization of both the pure oxides under air flow. These results pointed out the thermal stability of both Sb_2O_3 and Sb_2O_5 at a temperature of 850 °C under oxidative conditions.

Fig. 3. Antimony partitioning during the thermal treatment of pure mineral compounds at 850 °C (Sb_2O_3, Sb_2O_5 and $SbCl_3$).
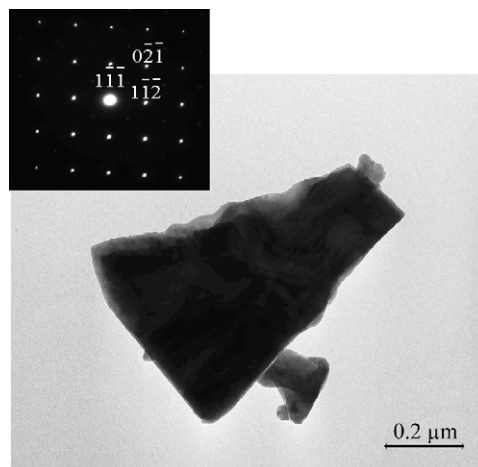

Fig. 5. TEM micrograph of the bottom ashes after the thermal treatment at 850 °C of pure Sb_2O_3 and related SAED pattern.

Speciation study was performed during the laboratory-scale experiments on pure Sb_2O_3 at 850 °C in the quartz furnace, showing that 100% of the initial amount of antimony was trapped in the scrubber solutions under the oxidation degree +III.

The important volatilization of antimony from Sb_2O_3 at 850 °C (62%) observed in our laboratory furnace allowed us to confirm that only moderate oxidative conditions were present in the fuel licked bed, as hypothesized earlier. Indeed, as shown by Paoletti et al. by TGA [9], in total scarcity of air, under nitrogen, Sb_2O_3 started to volatilize at about 600 °C and the sample was completely volatilized at about 870 °C, after around 50 min under thermal constraint, if considering a heating temperature rate of 5 °C min^{-1}. In our case, Sb_2O_3 was only partly volatilized (62%), indicating either moderate oxidative conditions in the fuel bed, and/or insufficient residence time to allow full gas-phase mass transfer.

By contrast, the whole amount of $SbCl_3$ placed in the thermal treatment device was volatilized, and more than 72% of the total antimony introduced was found back in the scrubbing device, while 27% of antimony was condensed on the reactor's walls. Less than 1% remained in bottom ashes. Such a result was expected, based on $SbCl_3$ boiling temperature (283 °C), which is far below the lowest temperature applied in our experimental thermal treatment device (850 °C). Such experimental results are consistent with previously reported thermodynamic computational data [9].

3.2. Thermal treatment of a Sb-rich halogenated industrial waste

3.2.1. Antimony mass balance

Table 1 shows the antimony mass balance and speciation determined after the thermal treatment of the halogenated waste at 850 °C and 1100 °C. The proportion of volatilized antimony was substantially the same at both the tested temperatures, close to 63% (Table 1). Relative proportions remaining in bottom ashes were also similar for both temperatures with values close to 36%. Antimony present in the waste showed a similar behaviour compared with Sb in pure Sb_2O_3 at 850 °C, with partitioning between gas and ashes in the same order of magnitude (volatilized: 62%, bottom ashes: 38%, Fig. 3). These results suggested that, despite a nX/nSb molar ratio far higher than the stoichiometric value required to form SbX_3 ($nX/nSb = 11$, with X: Cl or Br), in our experimental device the reaction of Sb_2O_3 with the halogens initially present in the waste was limited, confirming once again our hypothesis of low oxidative strength and too short residence time in the laboratory furnace. Indeed, it is thought that chlorination of antimony takes place slowly, mainly in the solid phase at temperature below 300 °C and only in strict oxidative conditions, with large excess of air [1,4,9,26]. It was also reported that under reducing conditions (pyrolysis), Sb_2O_3 synergist did not react with some brominated compounds in vacuum in the early step, but first evaporated as the dimer Sb_4O_6 [26].

A thermogravimetric experiment was performed on the pasty Sb-halogenated waste under oxidative conditions to approach its thermal behaviour in incineration conditions. The thermogram presented in Fig. 4b shows a first mass loss of about 50% between 20 °C and 150 °C, probably due in part to dehydration, the waste containing 30.9% of water. Further 30% of mass loss was observed between 150 °C and 550 °C, with no further volatilization at higher temperatures. Amount of antimony in the residual ashes from TGA measured by FAA was 2%, this value being close to those found in the licked bed experiments (Table 1). Thus, in incineration conditions, 82% of the waste mass is expected to be volatilized, while 18% would remain in the bottom ashes.

As a significant amount of bromine was present compared to chlorine in our waste (~9% Br vs 0.55% Cl), leading to a molar ratio nBr/nSb equal to 9, the specific fate of bromine may be discussed. This point was checked by using the thermodynamic software HSC chemistry for Windows 5.0 [27]. Inputs for thermodynamic calculations were those described by Diaz-Somoano et al. [28] in which chlorine element was substituted by bromine.

Diaz-Somoano et al. studied the behaviour of some metals in the combustion atmosphere during co-combustion processes of bio-waste materials and coal, using only thermodynamic equilibrium calculations [28,29], and without taking into account the kinetic phenomena. Influence of parameters such as temperature and flue-gas composition was evaluated on equilibrium composition in the combustion atmosphere. Based on such calculations, antimony should be totally volatilized at temperature higher than 600 °C under the speciation of SbO(g), while at lower temperatures only condensed oxides should form (SbO_2, Sb_2O_4 and Sb_2O_5). The presence of HCl (g) or H_2S(g) in the atmosphere should favour the formation of antimony halides and sulphides (SbCl(g), $SbCl_3$(g), Sb_3S_2(g), Sb_4S_3(g)) in the temperature range 200–500 °C. Above 500 °C, halides and sulphides are not stable and SbO(g) should be the main antimony species, whatever the partial pressure of oxygen in the atmosphere. In these studies, the formation of halides and sulphides of antimony were possible at equilibrium between 200 °C and 500 °C with very large excesses of chlorine and sulfur, ratio values of nCl/nSb and nS/nSb being higher than 1500 [28,29].

In our calculations, the substitution of chlorine by bromine under HBr or Br_2 forms did not change equilibrium compositions, with SbO(g) being the major antimony species at temperatures above 500 °C. The formation of $SbBr_3$(g) was possible in a temperature range from 200 °C to 500 °C, when the molar ratio nBr/nSb was very high, with values close to 1200. In these conditions, only 1.6% of initial antimony was under the halide form in the gas-phase.

Those calculations support previous findings, indicating that during oxidative thermal treatment of flame retardants halogenation of antimony takes place mainly in the solid phase at temperature below 300 °C.

Watanabe et al. [26] performed laboratory-scale experiments focusing on the volatilization of Sb from a mixed combustible prepared with Sb_4O_6 and highly chlorinated solid residues. The trials carried out at 500 °C and 700 °C using a quartz furnace with licked bed similar to the one we used herein showed that, despite nCl/nSb molar ratios above 25, the transfer of antimony to the gas-phase did not dominate in presence of excess chlorine. After 20 min of thermal treatment, antimony was also reported to partition between the gas (32%) and the residual solid phase (68%), highlighting a competition between transfer mechanisms based on volatilization and solidification within the solid residue. Reasons of the low transfer of antimony in the gas-phase during the experiments conducted by Watanabe et al. might also be attributed to the limited oxidative conditions and/or residence time under thermal constraint of their tests, as confirmed also by the high rate of volatilization they obtained on the quartz furnace with Sb_4O_6 reagent (81% at 500 °C). Sb_4O_6 is known to sublimate in vacuum above 400 °C, but not to vaporize below 900 °C under oxidative thermal treatment conditions [1].

Fate of antimony was also studied by Paoletti et al. in the 250 kg/h solid waste incinerator TAMARA in Karlsruhe (Germany)

Table 1

Overall results of the thermal treatment trials conducted on the Sb-rich halogenated waste at 850 °C and 1100 °C.

Temperature (°C)	850	1100
Proportion of ashes (%, dry weight)	12.3	11.3
Sb-content in ashes (g/100 g, dry weight)	4.1	4.6
Mass proportion of volatilized Sb with respect to total Sb introduced (%, dry weight)	64.5	63.4
Mass proportion of unvolatilized Sb, remaining in the bottom ashes, with respect to total Sb introduced (%, dry weight)	35.5	36.6
Sb III/Total volatilized Sb (%)	86	59

[9], with a residence time of 80 min. Experiments in which $SbCl_3$ and Sb_2O_3 were added to spike the feed (a mixture of plastic materials) showed high volatilization of antimony out of the fuel bed. Antimony was not found in the filtered flue-gas. Main partitioning concerned grate and fly ashes, with percentage values close to 45–50% for all the spiking additives (Sb_2O_3, $SbCl_3$, $Sb_2O_3 + PVC$). From a theoretical point of view it was expected that antimony volatilized by means of halogenation processes, but the experimental findings did not support this prediction, suggesting a competition between volatilization and solidification. Paoletti et al. suggested the presence or the formation of antimonates in the fuel bed as a possible reason for the fixation of antimony in the bottom ashes. The reaction between antimony trioxide and alkaline-earth elements in presence of oxygen is indeed thermodynamically possible, generating antimonate salts that are extremely stable under thermal constraint [9].

In the waste combustible studied herein, the overall content of alkaline-earth elements was too low compared with the high amount of Sb available (<1% for alkaline-earth elements and 1.46% for Sb, respectively). The trapping of antimony under the form of antimonates during the thermal treatment process could occur, but it could not fully explain our results.

Fig. 6 shows the distribution of the antimony recovered from the experimental thermal treatment of the halogenated waste, in the reactor and in the trapping devices. The term "reactor" corresponds to the sole antimony recovered during the washing of the quartz reactor, without taking into account the amount of Sb present in the bottom ashes. Before being able to obtain a coherent antimony mass balance at a temperature of 850 °C, many preliminary waste thermal treatment trials (>5) were necessarily conducted. Indeed, during these preliminary tests, the mass balance calculations for antimony always widely exceeded 100%, probably due to the condensation of gaseous antimony compounds on the coldest surfaces of the device, resulting in a contamination of the successive experiments. An adapted decontamination protocol was required to clean the experimental device, allowing a total elimination of the Sb-contamination. In their experiments focusing on the volatilization of solid Sb_4O_6 under air flow at 700 °C, Watanabe et al. [26] observed a similar phenomenon of Sb-deposit on the walls of the quartz reactor, and such contamination could not be removed by aqua regia.

The antimony concentration of the solution in scrubber no. 6 (1% of the total antimony introduced in the system) is twenty eight times lower than the solution contained in scrubber no. 5. This result, accordingly to the French standardized method NF EN 14385, indicates a high efficiency of the trapping system used in this study [20].
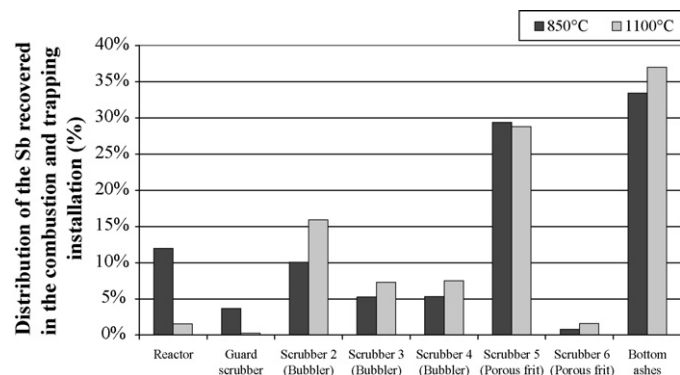
At 850 °C, 15% of the total antimony introduced in the system was found back on the walls of both the reactor and the first guard flask, probably due to fast condensation of gaseous antimony compounds on chilled surfaces, while this phenomenon was limited at 1100 °C, concerning only less than 2% of total antimony. Consistently, at 1100 °C the antimony was volatilized, but not fastly recondensed on the walls, and then captured in a major proportion in flask no. 2 compared with the Sb retained in the same location at 850 °C (15% *vs.* 10% of the initial quantity of Sb introduced). In the scrubbing solutions from flasks no. 3, 4 and 5, the trapping profiles were comparable at both the studied temperatures, with always a slightly increased efficiency at 1100 °C. Whatever the temperature, the use of a porous nozzle greatly improved the trapping efficiency (flask no. 5).

3.2.2. Determination of antimony oxidation degree in flue-gases

By studying through polarography and anodic stripping voltamperometry the flask scrubbing liquids and the washing solutions generated by the walls decontamination procedure, oxidation degrees of the antimony emitted in the gas-flow upon treatment were determined. Determining the oxidation degree of antimony in the solid phases (raw waste, ashes...) was not possible, as such an analysis would require hot digestion with highly oxidative nitric acid, inducing the biased conversion of all the antimony forms in presence to the highest degree of oxidation +V.

Table 1 gives the respective proportions of Sb(III) and Sb(V) in the flue gas stream at both temperatures. As previously mentioned, the proportion of residual antimony in the ashes after treatment was similar at both the tested temperatures (36% and 37% of the initially introduced amount of Sb). The total fraction of antimony transferred to the gas-phase through volatilization was also almost identical at 850 °C and 1100 °C (64% and 63%, respectively). However, the relative proportion of Sb(III) in the gas-phase decreased with an increase in temperature, with values of 86% and 59%, at 850 °C and 1100 °C, respectively (Table 1). On the contrary, the amount of Sb(V) in the gas-phase was far much important at 1100 °C with respect to 850 °C (41% and 24% respectively).

The increased proportion of Sb(V) in the exhaust gas during the thermal treatment of the Sb-rich halogenated waste at 1100 °C could be explained (i) by an oxidation in the strongly oxidative gas-stream, *post*-combustion, of the antimony probably evaporated under a +III valence form due to partial local reducing conditions in the licked bed, and/or, (ii) by the formation of SbX_5 species (with X: Cl or Br) through complex halogenation reactions in the solid phase. In case of a prevalence of the latter mechanism, the consumption of halogens through reaction with Sb would be 1.7 times greater at 1100 °C with respect to 850 °C. Such mechanism seems however unlikely, due to local low oxidative conditions in the fuel bed and short residence time.

The amount of antimony evaporated at both temperatures (~60%) is congruent with the speciation of Sb in the raw waste (under the form Sb_2O_3) as well as with the results obtained from the test on pure Sb_2O_3, suggesting poor interaction in the raw solid waste between the trioxide and the other components of the matrix, probably due to scarcity of oxygen and limited reaction time. As previously reported, 100% of the initial amount of antimony was trapped in scrubber solutions under the oxidation degree +III during thermal treatment tests performed at 850 °C with pure Sb_2O_3. In our experimental system, increasing the temperature from 850 °C to 1100 °C did not modify the proportion of gaseous Sb_2O_3 emitted in the gas-phase, but within the gas-stream a major conversion of antimony to its +V valence occurred at the highest temperature (1100 °C), probably by a strong thermal oxidation in the *post*-combustion phase.

Results obtained by XRD of residual bottom ashes after the thermal treatment at 1100 °C did not point out the presence of any Sb
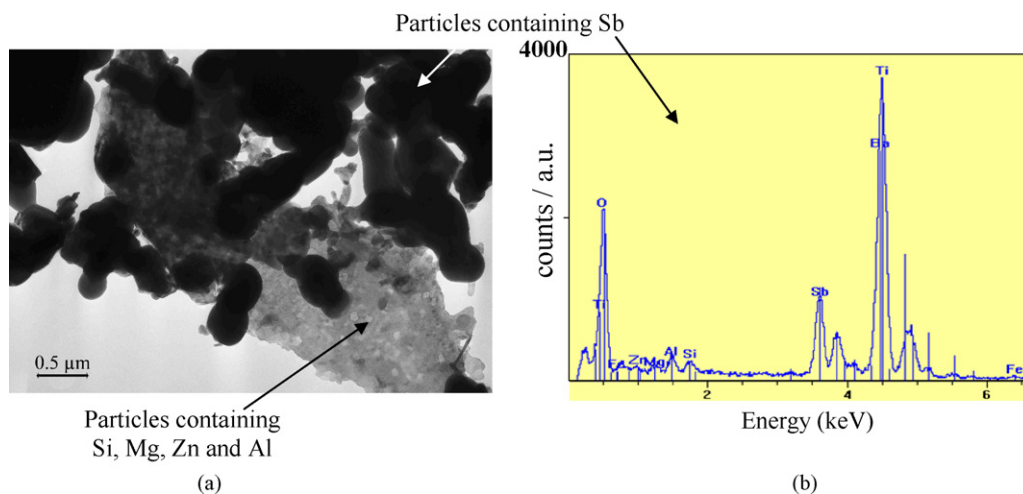

Fig. 6. Distributions of Sb within the different compartments of the experimental device during the thermal treatment of the Sb-rich halogenated waste.

Fig. 7. (a) Bright-field TEM micrograph of the two types of particles of the bottom ashes after the treatment at 1100 °C of the halogenated waste, and (b) EDXS analysis of the particles containing antimony.

crystallographic phases, but the presence of antimony in the bottom ashes was confirmed by TEM observations. Qualitative information could be derived from EDXS analysis and indicated the presence of two main kinds of particles, with different chemical composition: (i) particles bearing Sb, containing also O, Ti and Ba (EDX spectrum and corresponding TEM micrograph shown on Fig. 7), and (ii) particles containing Si, Al, Mg, Zn, O, without Sb. EDXS analysis performed on numerous particles of the bottom ashes after the thermal treatment of the halogenated waste, confirmed that antimony was always associated with barium and titanium. Unfortunately, XRD measurements and TEM characterization observations could not allow to determine the oxidation degrees of Sb in bottom ashes.

4. Conclusions

By using in series atomic absorption spectrometry, polarography/voltamperometry and microwave digestion, the mass balance as well as the oxidation degree of the antimony emitted in the exhaust-gas during the thermal treatment of three pure single Sb-species (Sb_2O_3, Sb_2O_5 and $SbCl_3$), and of a Sb-rich halogenated hazardous waste were studied. Our experimental thermal treatment device combined low oxidative strength in the licked waste-bed, but high oxidative and high temperature conditions in the *post*-combustion zone of the furnace.

The results related to the volatilization of the three pure Sb-species were in agreement with their respective physical–chemical properties and with the experimental conditions applied. The antimony was more volatile when associated with chlorine in $SbCl_3$ than if present under the form of an oxide. Under our moderate oxidative conditions in the fuel bed, antimony pentoxide was not evaporated, while the trioxide presented an intermediate behaviour, partitioning with constancy between the bottom ashes (64%) and the gas-phase (36%) at both tested temperatures (850 °C and 1100 °C).

Antimony mass balance measurements performed after short-time thermal treatment of the Sb-rich halogenated waste at both the tested temperatures showed that increasing the temperature of 250 °C did not favour the transfer of antimony, present mainly in the raw waste under the form of Sb_2O_3, to the gas-phase. The proportion of antimony remaining in the bottom ashes represented 36%, at 1100 °C, as well as at 850 °C. Despite a halogen/antimony molecular ratio far above the required stoichiometry in the raw waste, it appeared that in our experimental device the interactions between these halogens and antimony trioxide were limited in the

solid matrix, probably due to partially reducing conditions in the fuel bed as well as to insufficient residence time under thermal constraint.

However, if the volatilization of antimony was comparable at both temperatures in our experimental furnace, an increase of 250 °C significantly and undoubtedly promoted the presence of Sb(V) rather than Sb(III) in the *post*-combustion zone. Given the increased toxicity of the different Sb(III) forms compared to Sb(V) species, this result is of great importance when considering the functioning of a full-scale industrial incineration plant. Thermal treatment at a higher temperature (1100 °C) indeed allowed a major conversion of Sb(III) to Sb(V) in the gas-phase, thus resulting potentially in an increased detoxification of the flue-gas stream. In addition, it was evidenced herein that during the thermal treatment at low temperature (850 °C) of Sb-rich residues, Sb-species were able to settle and accumulate in various chilled parts of a thermal treatment device, resulting in a contamination. At a laboratory-scale, specific cleaning procedures helped curbing the contamination. On a full-scale industrial plant in which such wastes would be incinerated at 850 °C, such decontamination measures would be very difficult to implement. All these data suggest that the Sb-rich wastes, containing especially Sb_2O_3, should be treated in a specialized hazardous waste incineration plant, and necessarily at high temperature (1100 °C), whatever their halogen contents.

The trapping of antimony by acid solutions was effective in our study. Such effective gas-scrubbing conditions are also currently found on specialized hazardous waste incineration plants, which are also equipped with adapted processes and exutories for the treatment of soiled scrubbing solutions, APC residues and bottom ashes. It would be interesting now to study the operating conditions that would favour the trapping of the metalloid in the bottom ashes during incineration.

References

[1] S.M. Lomakin, G.E. Zaikov, New Concepts in Polymer Science: Ecological Aspects of Polymer Flame Retardancy, VSP, Utrecht, The Netherlands, 1999, 158 pp.

[2] J.H. Lau, C.P. Wong, N.C. Lee, S.W. Ricky Lee, Electronics manufacturing with lead-free, in: Halogen-Free and Conductive-Adhesive materials, McGraw-Hill, Hardcover, 2002, 700 pp.

[3] R. Mathys, J. Dittmar, C.A. Johnson, Antimony in Swittzerland, in: A Substance Flow Analysis, Federal Office for the Environment, 2001, p. 151.

[4] R. Dumler, D. Lenoir, H. Thoma, O. Hutzinger, Thermal formation of poly-brominated dibenzofurans and dioxins from decabromodiphenyl ether flame retardant: influence of antimony (III) oxide and the polymer matrix, Chemo-sphere 20 (1990) 1867–1873.

[5] J.L. Jurs, Development and Testing of Flame Retardant Additives and Poly-mers, U.S. Department of Transportation, Federal Aviation Administration, DOT/FAA/AR-07/25, 2007, 303 pp.

[6] E. Jakab, Md.A. Uddin, T. Bhaskar, Y. Sakata, Thermal decomposition of flame-retarded high-impact polystyrene, J. Anal. Appl. Pyrolysis 68–69 (2003) 83–99.

[7] F. Paoletti, H. Seifert, J. Vehlow, P. Sirini, Oxyanious forming elements in waste combustion–partitioning of antimony, Waste Manag. Res. 18 (2000) 141–150.

[8] F. Carpentier, S. Bourbigot, M. Le Bras, R. Delobel, M. Foulon, Charring of fire retarded ethylene vinyl acetate copolymer—magnesium hydroxide/zinc borate formulations, Polym. Degrad. Stab. 69 (1) (2000) 83–92.

[9] F. Paoletti, P. Sirini, H. Seifert, J. Vehlow, Fate of antimony in municipal solid waste incineration, Chemosphere 42 (2001) 533–543.

[10] W.S. Seames, J. Sooroshian, J.O.L. Wendt, Assessing the solubility of inorganic compounds from size-segregated coal fly ash aerosol impactor samples, J. Aerosol Sci. 33 (1) (2002) 77–90.

[11] Arrêté Ministériel NOR:DEVP0210352A, 2002, Arrêté du 20 septembre 2002 relatif aux installations d'incinération et de co-incinération de déchets dan-gereux, Journal Officiel de la République Française (280 du 1er Décembre) (2002) 19789–19801.

[12] Arrêté Ministériel NOR:DEVP0210351A, 2002, Arrêté du 20 septembre 2002 relatif aux installations d'incinération et de co-incinération de déchets non dan-gereux et aux installations incinérant des déchets d'activités de soins à risques infectieux, Journal Officiel de la République Française (280 du 1er Décembre) (2002) 19778–19789.

[13] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, Official Journal of the European Communities L 332/91-111.

[14] IUPAC, International Union of Pure and Applied Chemistry, Compendium of Chemical Terminology, 2nd ed., 1997.

[15] T. Gebel, Arsenic and antimony: comparative approach on mechanistic toxicol-ogy, Chem. Biol. Interact. 107 (1997) 131–144.

[16] M. De Boeck, M. Kirsch-Volders, D. Lison, Cobalt and antimony: genotoxicity and carcinogenicity, Mutat. Res. 533 (2003) 135–152.

[17] International Agency for Research on Cancer, Summary & Evaluations, http://www.inchem.org/documents/iarc/vol47/47-11.html.

[18] NF EN 14582, 2007. Norme Française. Caractérisation des déchets. Teneur en halogènes et en soufre. Combustion sous oxygène en systèmes fermés et méth-odes de dosage, Association française de normalisation, AFNOR, 26 pp.

[19] A. Khalfi, G. Trouvé, R. Delobel, L. Delfosse, Correlation of CO and PAH emissions during laboratory-scale incineration of wood waste furnitures, J. Anal. Appl. Pyrolysis 56 (2000) 243–262.

[20] NF EN 14385, 2004. Norme Française. Emissions de sources fixes, Détermination de l'émission totale de As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Ti et V, Association française de normalisation, AFNOR, 37 pp.

[21] S. Fendeleur, Métaux lourds et incinération de déchets industriels: spéciation et localisation des éléments métalliques dans les différentes phases (solides, liquides, gazeuses) issues du traitement, Thèse de Doctorat, Réseau Coopératif de Recherche sur les Déchets et l'Environnement (RE.CO.R.D), Université de Haute Alsace, 1999, 209 pp.

[22] SW846 Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils and oils, www.epa.gov/epawork/hazard/testmethods/sw846/pdfs/3051a.pdf, 2007.

[23] L. Rahman, W.T. Corns, D.W. Bryce, P.B. Stockwell, Determination of mercury, selenium, bismuth, arsenic and antimony in human hair by microwave diges-tion atomic fluorescence spectrometry, Talanta 52 (2000) 833–843.

[24] A.M. Bond, S. Kratsis, O.M.M.G. Newman, Determination of antimony(III) and antimony(V) in copper plant electrolyte by anodic stripping voltamperometry, Electroanalysis 9 (1997) 681–684.

[25] D. Orosel, P. Balog, H. Liu, J. Qian, M. Jansen, Sb_2O_4 at high temperatures, J. Solid State Chem. 178 (2005) 2602–2607.

[26] S. Watanabe, S. Inoue, H. Ito, Chlorine promotes antimony volatilization in municipal waste incineration, J. Mate. Cycles Waste Manag. 2 (2000) 10–15.

[27] A. Roine, HSC Chemistry Software for Windows Version 5.0, Outokumpu Resarch, 02103-ORC6T, www.outokumpu.com, 2002, Finland.

[28] M. Diaz-Somoano, S. Unterberger, K.R.G. Hein, Prediction of trace element volatility during co-combustion processes, Fuel 85 (2006) 1087–1093.

[29] M. Diaz-Somoano, M.R. Martinez-Tarazona, Trace element evaporation during coal gasification bases on a thermodynamic equilibrium calculation approach, Fuel 82 (2003) 137–145.