

Nobuhisa Watanabe · Saburo Inoue · Hisao Ito

Chlorine promotes antimony volatilization in municipal waste incineration

Received: July 2, 1998 / Accepted: January 28, 1999

Abstract

Antimony volatilization in municipal waste incineration was studied. Two municipal waste samples and antimony(III) oxide (Sb_2O_3) were heated to 500°C and 700°C in an air stream in a quartz furnace. The volatilization of Sb_2O_3 occurred more at 700°C than at 500°C. Conversely, antimony volatilization from municipal waste was stronger at 500°C than at 700°C. This implies that antimony from municipal waste is volatilized as chloride instead of oxide. The chlorine sources for antimony chlorination, a gas-phase reaction involving hydrochloric acid and a solid-phase reaction of inorganic chlorine, e.g., CaCl_2 , were compared. Only the solid-phase reaction could offer enough active chlorine to induce chlorination of antimony oxide.

Key words Antimony · Chlorine · Municipal waste · Incineration · Thermodynamics

Introduction

Metal volatilization in municipal waste incineration has been an important point of discussion for a long time.¹ Some metals which are treated during the metallurgical process at high temperature with no significant loss may be significantly volatilized in municipal waste incinerators. Chlorine contained in waste has been implicated in metal chloride production, but at the same time the stability of metal chlorides compared with that of oxides should be carefully considered.²

Although hydrochloric acid in the gas phase does not possess sufficient chlorine activity to maintain metal chlo-

rides, it should be noted that chlorine transfer in ash matrix could produce very high chlorine activity.³

We previously reported on the mass balance of antimony in a municipal waste incinerator, which presented 30%–70% of antimony partitioned to fly ash.⁴ The antimony partitioning in fly ash may be due to both volatilization of Sb_2O_3 and the production of SbCl_3 , the boiling point of which is 223°C. However, further experimental studies should be performed to clarify which reaction is dominant.

In this paper, an overview of the progress of antimony in municipal waste incinerators and the chlorine activity are introduced. An incineration experiment using two municipal waste samples is presented, the results of which are discussed according to partitioning mechanisms and chlorine activity.

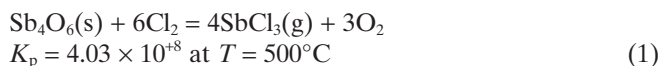
Theory

Pathways of antimony volatilization

The possible fate of antimony in an incinerator is illustrated in Fig. 1. Most of the antimony input to municipal waste incinerators is thought to be Sb_2O_3 . Volatile antimony compounds are Sb_2O_3 and SbCl_3 . Antimony(III + V) oxide (Sb_2O_4) and possible compounds with sample matrices, such as silicate or alumina, are nonvolatile. Here we exclude antimony(V) chloride (SbCl_5) because of its intense fragility.

The saturated vapor pressure of Sb_2O_3 is calculated using thermodynamic data from the *Materials-Oriented Little Thermodynamic Database 2 (MALT 2)*⁵ and presented in Fig. 2. It can be seen that the temperature range 500–600°C is the critical area of volatilization and ash deposit.

SbCl_3 is a rather volatile compound with a boiling point of 223°C. However, if we discuss the volatilization of SbCl_3 , the chlorination reaction must be taken into account:



N. Watanabe (✉) · S. Inoue · H. Ito
Osaka City Institute of Public Health and Environmental Sciences,
8-34 Tohjoh-cho, Tennohji-ku, Osaka 5430026, Japan
Tel. +81-6-6771-3354; Fax +81-6-6772-0676

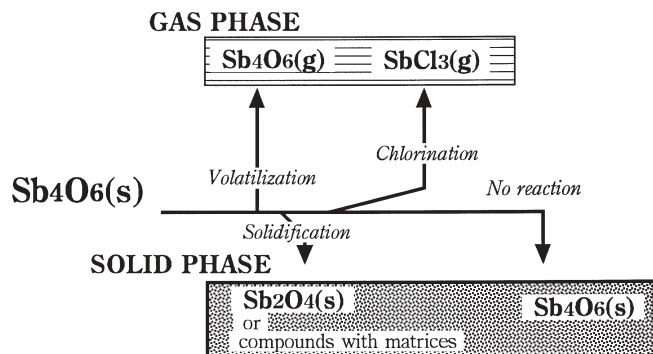


Fig. 1. Possible fate of antimony in a municipal waste incinerator

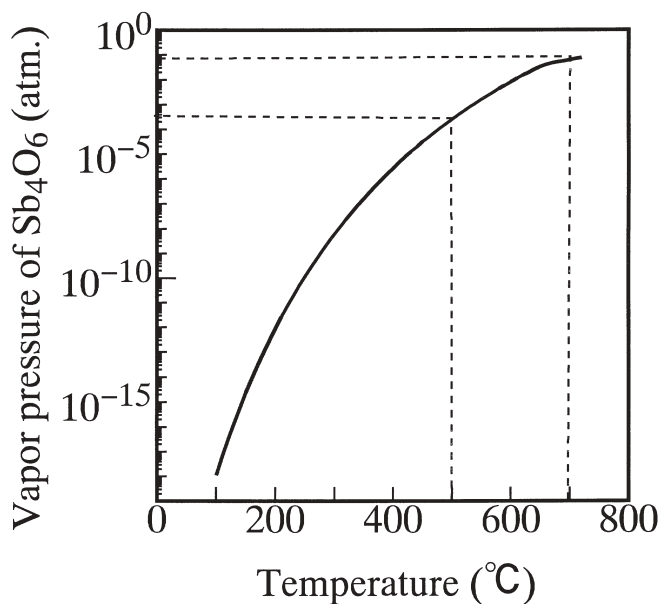


Fig. 2. Vapor pressure of antimony(III) oxide (Sb_4O_6). Chemical reaction: $\text{Sb}_4\text{O}_6(\text{s}) = \text{Sb}_4\text{O}_6(\text{g})$. Equation: $K_p = [\text{Sb}_4\text{O}_6(\text{g})]/[\text{Sb}_4\text{O}_6(\text{s})]$. Condition: $[\text{Sb}_4\text{O}_6(\text{s})] = 1$

Figure 3 shows the vapor pressure of SbCl_3 which is in equilibrium with $\text{Sb}_4\text{O}_6(\text{s})$ under variable Cl_2 concentration.

Chlorine activity

Although chlorine gas (Cl_2) cannot easily be detected in flue gas, it is well known that chlorination of compounds occurs. Current debate on dioxin formation^{6,7} suggests “oxychlorination,” which is typically expressed in the following reaction:



“Active chlorine” is available not only from hydrochloric acid in the gas phase, but also from chloride in the ash matrix. For example, calcium chloride will generate active chlorine when it is heated with silica:

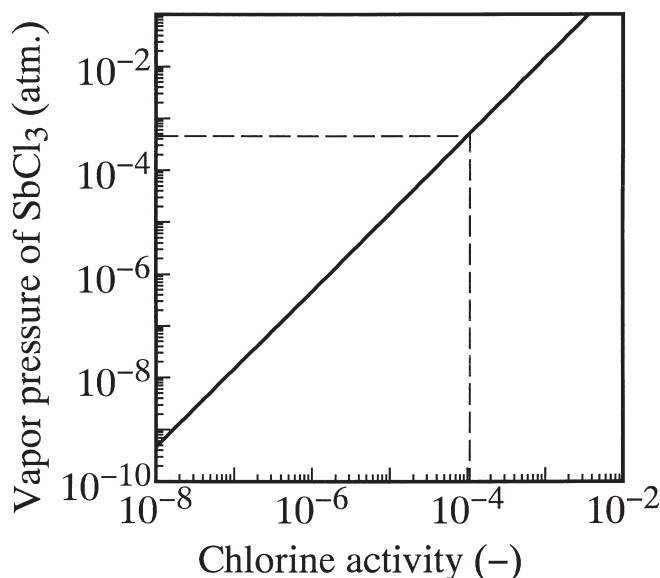
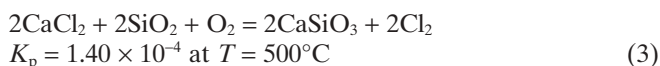


Fig. 3. Vapor pressure of antimony(III) chloride (SbCl_3) which is in equilibrium with antimony(III) oxide (Sb_4O_6) under variable chlorine activity. Chemical reaction: $\text{Sb}_4\text{O}_6(\text{s}) + 6\text{Cl}_2 = 4\text{SbCl}_3(\text{g}) + 3\text{O}_2$. Equation: $K_p = [\text{SbCl}_3(\text{g})]^4 [\text{O}_2]^3 / ([\text{Sb}_4\text{O}_6(\text{s})] [\text{Cl}_2]^6)$. Condition: $K_p = 4.03 \times 10^{+8}$ ($T = 500^\circ\text{C}$); $[\text{Sb}_4\text{O}_6(\text{s})] = 1$; $[\text{O}_2] = 0.2$

Table 1. Characteristics of samples

	Sample A	Sample B
Concentration of antimony ($\mu\text{g/g}$)	3712	480
Ash contents (-)	0.095	0.336
Concentration of chlorine (mg/g)	27.6	18.1



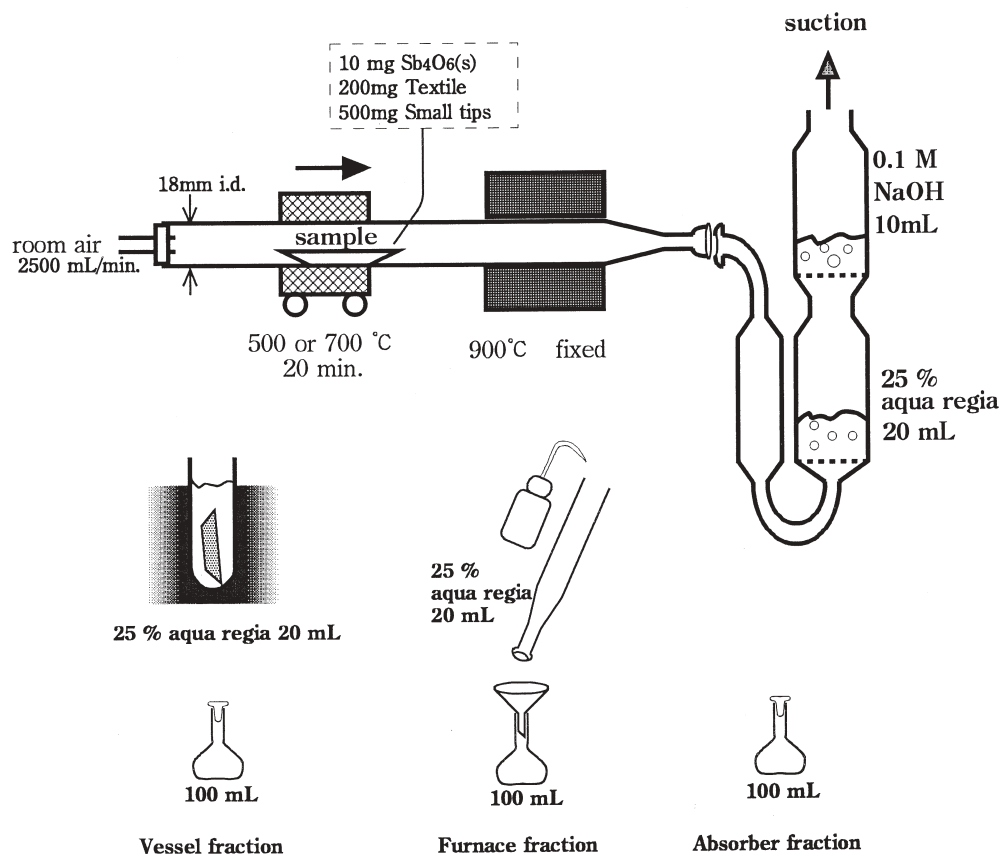
The aim of the chlorine activity argument is to compare “supplied chlorine activity” and “needed chlorine activity.” In order to induce a chlorine atom transfer reaction, “supplied chlorine activity” must be sufficiently higher than “needed chlorine activity.”

Methods and materials

Sample

Two samples, which contained a high concentration of antimony, were selected from an antimony municipal waste survey⁸ which was conducted with the sets of waste samples.⁹ Sample A was the “textile” from incinerator No. 8, and sample B was the “small tips (to pass a 5-mm screen)” from incinerator No. 2. The sample characteristics are given in Table 1. As a comparison with the municipal waste sample, antimony(III) oxide (Sb_4O_6) reagent was used.

Fig. 4. Experimental device and procedures



Quartz furnace

The incineration experimental device used is illustrated in Fig. 4. A quartz tube furnace was heated by a moving furnace (500°C or 700°C) and a fixed furnace (900°C). The oxidant gas was room air at 2500ml/min. The sample was mounted in a quartz vessel which was placed in the front of the moving furnace. With the moving furnace at a slow slide, the incineration was finished in 20min.

Gas absorber

Gas absorption was performed two steps: the front absorber was 20ml of 25% aqua regia (12M HCl 4ml + 14M HNO_3 1ml + water 15ml) and the back absorber was 10ml of 0.1M NaOH solution, whose purpose was mainly to protect the gas suction line and the pump.

Procedures

All the experiments were carried out in duplicate, with 10 mg of Sb_4O_6 , 200mg of sample A, and 500mg of sample B. After the sample incineration, the quartz vessel, the quartz furnace, and the absorber were separately treated (see Fig. 4). The quartz vessel was immersed in 20ml of 25% aqua regia in a test tube which was heated to boiling point. The

quartz furnace was rinsed with 20ml of 25% aqua regia followed by distilled water. All fractions were made up to 100ml each. Antimony concentration was measured by air-acetylene flame atomic absorption spectrometry.

Results and discussion

Total recovery

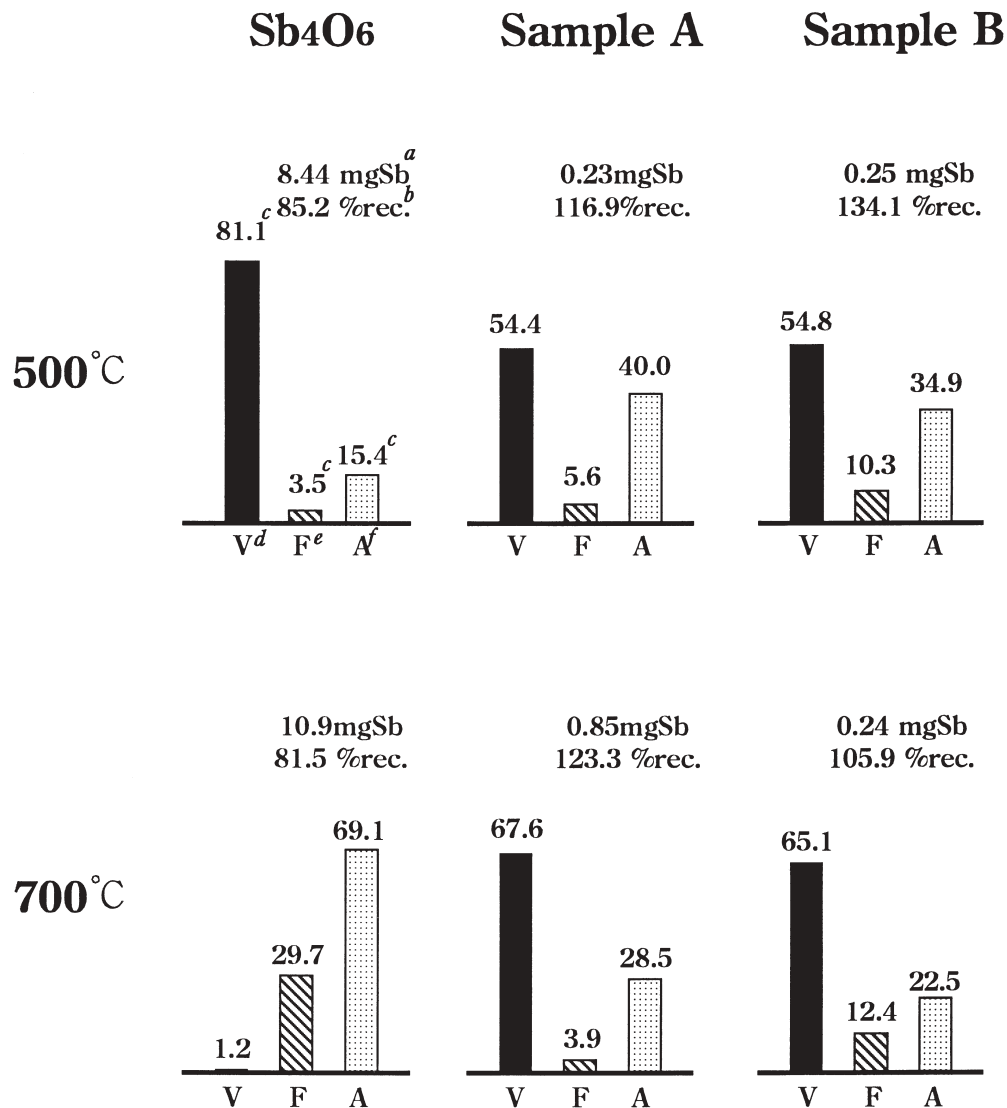
The experimental results are summarized in Fig. 5. In each graph, the relative percentages of antimony which were partitioned in the quartz vessel, the quartz furnace, and the absorber are presented. The total amount of antimony which was initially mounted on the quartz vessel and total recovery efficiency are also given.

Total recoveries in the experiment with waste samples were in the range 105.9–134.1%. This was probably due to the fact that the amount of sample was so small that the ratio of fine particles taken in the vessel became slightly higher than the original sample. Mounting a large amount of sample was not possible, as this would result in incomplete combustion.

Total recovery in the experiment with Sb_4O_6 was lower than 100%. A white deposit on the inner surface of the quartz furnace was observed, which was not dissolved in aqua regia. Hence, this white deposit could make the total recovery lower than 100%.

Fig. 5. Antimony partitioning to vessel, furnace, and absorber.

^aAmount of antimony initially mounted on the vessel. ^bTotal recovery efficiency. ^cPercentage of relative partitioning. ^dVessel. ^eFurnace. ^fAbsorber



Behavior of antimony(III) oxide

When Sb₄O₆ was heated to 500°C, up to 81% remained in the vessel (Fig. 5, footnote a), while as much as 98.8% was volatilized when heated to 700°C (Fig. 5, footnote b). Comparing these results with the vapor pressure calculation in Fig. 2, which indicates 2.6×10^{-4} and 6.5×10^{-2} (atm) at 500 and 700°C, respectively, the following deduction can be made: transfer to the gas phase will occur in ca. 20% of the material with a vapor pressure of 2.6×10^{-4} (atm), while a vapor pressure as high as 6.5×10^{-2} (atm) will result in complete volatilization.

Behavior of antimony from sample A

The antimony in sample A (“textile”) showed a significant volatile transfer even at 500°C. This suggests that some volatile antimony compounds other than Sb₄O₆(g) were

produced. We believe it is SbCl₃. When heated to 700°C, volatile transfer efficiency decreased. This means that volatilization and solidification are in competition, and at higher temperatures (700°C) solidification becomes more dominant.

In addition, it is thought that chlorination of antimony takes place slowly. If it were a fast reaction, the results should show no difference between the 500°C and 700°C experiments.

Behavior of antimony from sample B

The behavior of antimony from sample B (“small tips”) was similar to that from sample A. However, the probability of a reaction with ash matrix in sample B seemed to be somewhat higher than in sample A. It corresponds to the difference in ash contents of the two samples (see Table 1).

Formation of Sb_2O_4 or stable matrix-based nonvolatile compounds

As mentioned above, a prominent white deposit insoluble in aqua regia was observed in the experiment with Sb_4O_6 . This white deposit may be Sb_2O_4 , as Sb_2O_4 is insoluble in aqua regia. However, the white deposit was rare in the experiment with waste samples. This also supports the possibility of the formation of SbCl_3 during the incineration of waste samples.

Solidification into ash matrices were more common when the amount of ash was large. Antimony mixed with ash was easily recovered with aqua regia treatment. This suggested that the antimony remaining in the ash was not in the form of Sb_2O_4 but as other compounds in the ash matrices.

Where did the chlorine come from?

Comparison of the required and supplied chlorine activity

It was not possible to measure the actual vapor pressure of SbCl_3 in the experimental device. However, the vapor pressure should be related to the vaporization ratio from the quartz vessel. Since the vapor pressure of Sb_4O_6 at $T = 500^\circ\text{C}$ is 2.6×10^{-4} (atm) with a vaporization ratio of 20%, we estimated the actual vapor pressure of SbCl_3 at 500°C to be 5×10^{-4} (atm) with a vaporization ratio of 50%. The calculation of SbCl_3 formation from $\text{Sb}_4\text{O}_6(\text{s})$ (see Fig. 3 and Table 2) suggests that 1.0×10^{-4} of chlorine activity is in equilibrium; in other words, 1.0×10^{-4} is the required chlorine activity.

The first step in a search for a chlorine source should be the evaluation of the gas-phase reaction with eq. 2. All calculation conditions are listed in Table 2. The moisture and oxygen gas are from the ambient air. To estimate the hydrochloric (HCl) concentration in the furnace, it is assumed that all the chlorine in the sample would turn into HCl, which would generate an average HCl concentration of 78 p.p.m. (v/v) for sample A. A peak concentration as high as 1000 p.p.m. may also occur. The calculated chlorine activity was in the range 3.8×10^{-7} – 6.3×10^{-5} , which is comparable to or lower than the concentration needed to induce chlorination of $\text{Sb}_4\text{O}_6(\text{s})$.

Solid-phase chlorine transfer is very strong. Inorganic chloride, which usually exists in municipal waste, can react with ash matrices such as silica and alumina. Equation 3 can be considered as a typical reaction. This reaction will generate a chlorine activity of 5.3×10^{-3} (see Table 2), which is sufficiently higher than the required chlorine activity (Fig. 6).

So far, the estimation makes it clear that chlorine from the solid-phase reaction is the most active. There is enough margin between the supplied chlorine activity and the required chlorine activity to drive chlorine atom transfer.

Equilibrium argument

It is also valuable to consider the theoretical values of the vapor pressure of SbCl_3 . Combining eqs. 1 and 2 gives eq. 4.

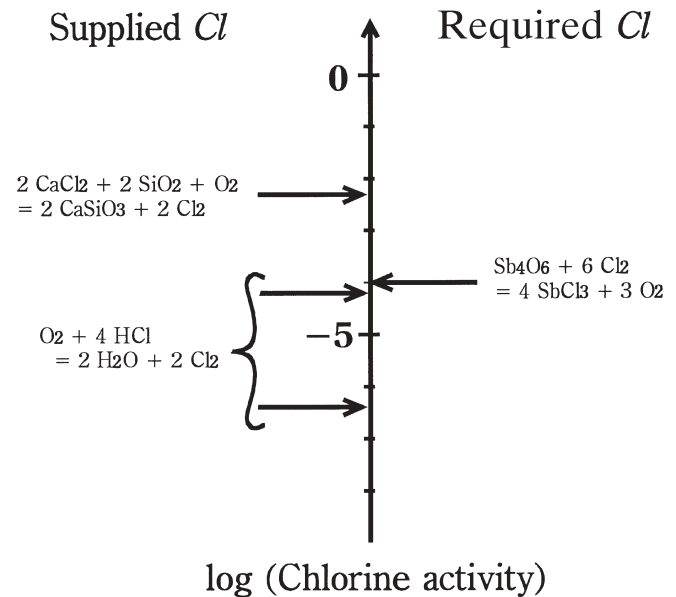


Fig. 6. Supplied and required chlorine activity

Table 2. Calculation of chlorine activity

Required chlorine activity		
$\text{Sb}_4\text{O}_6(\text{s}) + 6\text{Cl}_2 = 4\text{SbCl}_3 + 3\text{O}_2$		$K_p = 4.03 \times 10^{+8}$ at $T = 500^\circ\text{C}$
Condition: $[\text{Sb}_4\text{O}_6] = 1$; $[\text{SbCl}_3] = 5 \times 10^{-4}$; $[\text{O}_2] = 0.2$		
Result: $[\text{Cl}_2] = 1.0 \times 10^{-4}$		
Supplied chlorine activity		
$\text{O}_2 + 4\text{HCl} = 2\text{H}_2\text{O} + 2\text{Cl}_2$		$K_p = 7.58$ at $T = 500^\circ\text{C}$
Condition: $[\text{O}_2] = 0.2$; $[\text{H}_2\text{O}] = 0.02^a$; $[\text{HCl}] = (78\text{--}1000) \times 10^{-6}$		
Result: $[\text{Cl}_2] = 3.8 \times 10^{-7}$ – 6.3×10^{-5}		
$2\text{CaCl}_2 + 2\text{SiO}_2(\text{silicalite}) + \text{O}_2 = 2\text{CaSiO}_3(\text{wollastonite}) + 2\text{Cl}_2$		$K_p = 1.40 \times 10^{-4}$ at $T = 500^\circ\text{C}$
Condition: $[\text{CaCl}_2] = 1$; $[\text{SiO}_2] = 1$; $[\text{O}_2] = 0.2$; $[\text{CaSiO}_3] = 1$		
Result: $[\text{Cl}_2] = 5.3 \times 10^{-3}$		

^aEqual to a relative moisture content of 64% at room temperature (25°C)

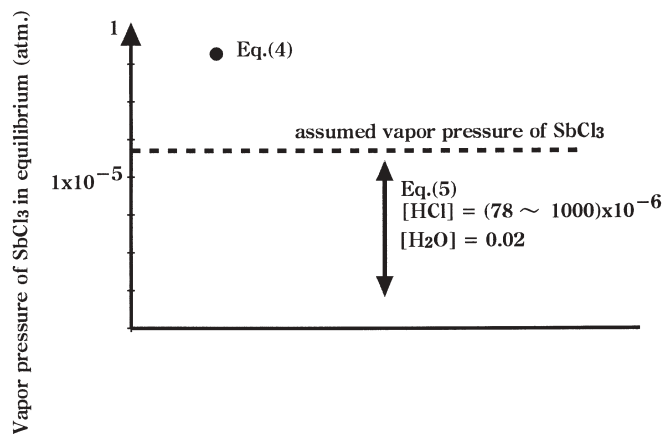
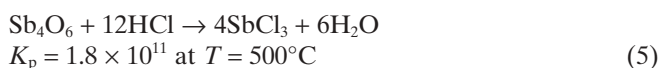


Fig. 7. Vapor pressure of SbCl_3 in the equilibrium calculation

In the same way, eqs. 1 and 3 give eq. 5.



Equation 4 would give $[\text{SbCl}_3] = 0.2$ if the other solid compounds were of activity one. Equation 5 would give $[\text{SbCl}_3] = 1 \times 10^{-7} - 2 \times 10^{-4}$ if $[\text{HCl}]$ were $78 - 1000 \times 10^{-6}$ with $[\text{H}_2\text{O}] = 0.02$. These values are plotted in Fig. 7, with the assumed vapor pressure of SbCl_3 from the experimental results (dotted line). The vapor pressure of potentially generated SbCl_3 from eq. 4 has a sufficient margin from the experimentally estimated vapor pressure. At the same time, the occurrence of SbCl_3 (from eq. 5) is comparable to or lower than the experimentally estimated value. Consequently, via eq. 4 is a more feasible way to generate SbCl_3 than via eq. 5.

It is important to discuss the effect of O_2 and H_2O in SbCl_3 formation via eq. 4 and eq. 5, as the concentrations of O_2 and H_2O in the present experiment were different from those in actual incinerators. In eq. 5, when the H_2O activity is increased, the reaction shifts to the left. The moisture content in the experimental device was 2%, while a typical moisture content in actual incinerators is 10–20%. Therefore, the possibility of SbCl_3 formation via eq. 5 in actual incinerators will be smaller than that in the experiment, although eq. 4 is not affected by H_2O .

Will antimony carry chlorine?

It is also clear that the SbCl_3 generated is too great for gas-phase chlorine activity. This entails gas-phase antimony in the solid phase. In addition, when SbCl_3 turns into oxides, considerable chlorine activity should be released. This chlorine transfer mechanism, i.e., “chlorine carried by metals,” could be a potential chlorine source for organochlorine compounds generated in municipal waste incinerators, since this

mechanism is expected to occur for other metal elements as well.

Conclusions

The antimony volatilization mechanism in municipal waste incineration was studied. Antimony(III) oxide (Sb_2O_3) and two waste samples (“textile” and “small tips”) were incinerated in an air-stream at 500°C and 700°C . In the Sb_2O_3 experiment, the ratio transported to the gas phase at 500°C was less than 20%, but at 700°C most of the antimony was volatilized. For both municipal waste samples, 45% of the antimony was transferred to the gas phase at 500°C . When waste samples were heated to 700°C , volatilization was suppressed. This suggested that antimony in waste could volatilize in the form of chloride (SbCl_3), and that volatilization and solidification are in competition.

Hydrochloric acid in the gas phase and inorganic chlorine in the solid phase were compared in terms of chlorine activity for a chlorine source. Hydrochloric acid in the gas phase would produce less than the required chlorine activity to generate enough SbCl_3 . However, the reaction of calcium chloride, silica, and oxygen would potentially offer more chlorine activity than is required. Inorganic chlorine in ash is thought to be the chlorine source generating SbCl_3 . As the SbCl_3 generated in the solid phase is in excess of the hydrochloric acid in the gas phase, it will again release active chlorine atoms. This may act as a potential chlorine source for the production of organochlorine compounds in municipal waste incinerators.

Acknowledgment This work was financed by the Japan Society of Waste Management Experts.

References

- Law SL, Gordon GE (1979) Sources of metals in municipal incinerator emissions. *Environ Sci Technol* 13:432–438
- Fernández MA, Martínez L, Segarra M, Garcia JC, Espiell F (1992) Behavior of heavy metals in combustion gases of urban waste incinerators. *Environ Sci Technol* 26:1040–1047
- Kubota H, Uchida S, Tsubone S, Katayama S, Tsuchiya K, Suzuki T, Inukai S, Kamo H (1982) Volatile chlorine in municipal waste (in Japanese). *J Solid Liq Waste* 12(8):15–23
- Watanabe N, Inoue S, Ito H Mass balance of arsenic and antimony in municipal waste incinerators. *J Mater Cycles Waste Manag* 1(1):38–47
- Nihon Netsu Sokutei Gakkai (1992) Thermodynamic database “MALT2” (in Japanese). Kagakugijyutsusha
- Addink R, Olie K (1995) Mechanism of formation and destruction of polychlorinated dibenzo-p-dioxine and dibenzofurans in heterogeneous systems. *Environ Sci Technol* 29:1425–1435
- Ismo H, Kari T, Juhani R (1997) Formation of aromatic chlorinated compounds catalyzed by copper and iron. *Chemosphere* 34:2649–2662
- Watanabe N, Inoue S, Ito H (1997) Antimony survey in municipal waste. III. Investigation of combustible compounds. *Environ Sanitary Eng Res* 11(3):37–41
- Watanabe N, Ito H (1997) Waste analysis for combustion process: the case of Osaka City, Japan. *Resource Conserv Recycl* 20:57–69