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Mass balance of arsenic and antimony in municipal waste incinerators

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Abstract

The arsenic and antimony balance in two municipal waste incinerators was investigated. Initially, the production rates of ash and wet scrubber effluent were estimated. Then the arsenic and antimony in the ash and wet scrubber effluent were determined, which gave an estimate of the elemental balance. The total amounts of arsenic and antimony in the municipal waste were 0.9 g/t and 30–44 g/t, respectively. The distributions to fly ash were 45–47% and 33–74% for arsenic and antimony, respectively. The distribution mechanisms of arsenic and antimony are discussed from the viewpoints of their thermodynamics as well as their initial valencies, which greatly affect their behaviour.

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

Introduction

Municipal waste incinerators receive various metals. As a result, the ash from municipal waste incinerators includes considerable concentrations of those metals. In order to obtain a general view of the elemental balance, not only the metal concentrations in the ash and effluent, but also their production rate should be taken into account. Unfortunately, in some studies, information on ash production rates is not combined with data on the metal concentrations in the ash. This is said to be due to the complexity and difficulty of the mass balance estimation.

Metal distributions between bottom ash and fly ash in municipal waste incinerators has been a subject of interest for a long time. In most cases, metal volatilization has been discussed in terms of boiling points, or of the competition between chloride and oxide formation. These attempts have

successfully explained the general behavior of many kinds of metal, but some exceptions were also recognized. Arsenic and antimony are typical exceptional elements.

Waterland et al.¹ obtained a contradictory result compared with their initial prediction for arsenic behavior, i.e., that most of the arsenic remained in the bottom ash, although the boiling point of arsenic oxide is rather low. They suggested the adsorption of arsenic into the clay/ash matrix. Fernández et al.² have shown that the competition between chloride and oxide formation would determine this behavior. However, these authors hardly mentioned arsenic and antimony, presumably because of their additional properties. In the case of antimony, the nonvolatile compound antimony oxide (Sb_2O_4) is rather more stable than antimony chloride (SbCl_3).³ The argument given by Fernández et al. would result in antimony remaining in the bottom ash, but in fact the opposite was observed.

Arsenic and antimony are important elements from a health and environmental perspective. We investigated antimony occurrence in municipal waste.^{4,5} Clarification of the elemental balance and behavior mechanisms is urgently needed. We present here, first an estimation of the ash and wet scrubber effluent production in two municipal waste incinerators, followed by chemical analysis and elemental balance calculations. We then discuss the occurrence and behavior of arsenic and antimony using thermodynamics.

Methods

Site description

Two incinerators (T-incinerator and N-incinerator), which are controlled by Osaka City, were investigated. They incinerate mainly household waste, and their capacities are nominally 600 t/day each. The average constituents of the waste are described in elsewhere.⁶ Essentially, the ash content in raw waste was 164.0 kg ash per t raw waste.

A diagram of the T-incinerator is given in Fig. 1. The exhaust gas is treated by an electrostatic precipitator (ESP) and a wet scrubber. Amounts of ash, gas, and effluent are

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Fig. 1. Mass flow diagram for the T-incinerator. *a*, electrostatic precipitator; *b*, wet scrubber; *c*, reheater. Result of sieve analysis: $\{M_{T(3)} + M_{T(2)}\}/M_{T(1)} = 25.1/49.0$ (see Table 1). The balance of arsenic and antimony is given in Table 3

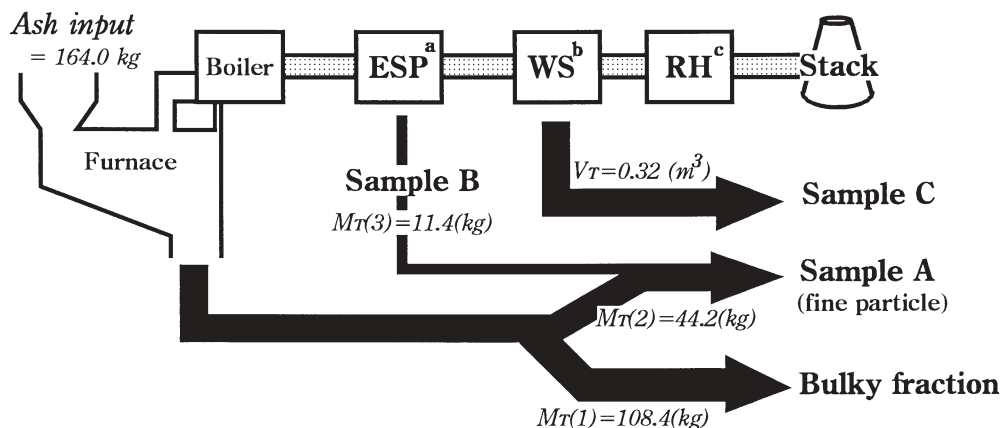
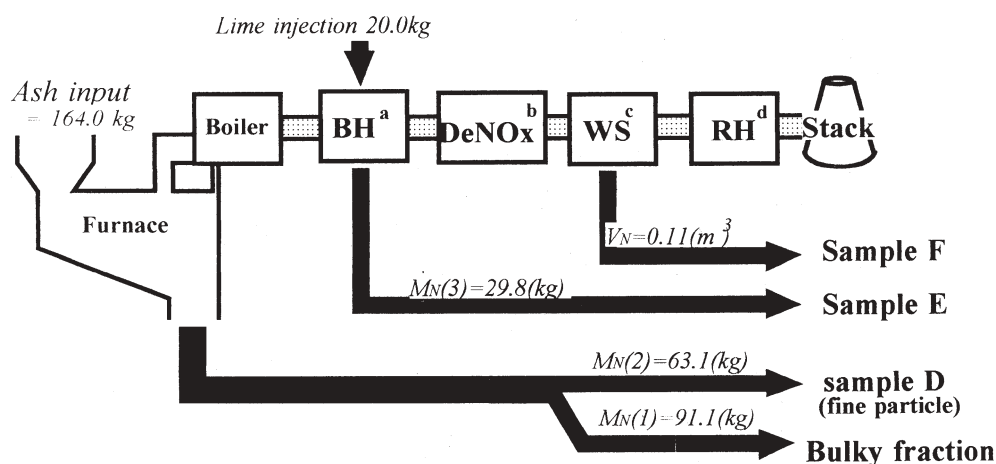


Fig. 2. Mass flow diagram for the N-incinerator. *a*, bag house; *b*, NO_x destruction catalysis; *c*, wet scrubber; *d*, reheater. Result of sieve analysis: $M_{N(2)}/M_{N(1)} = 28.6/41.3$ (see Table 2). The balance of arsenic and antimony is given in Table 4



expressed per one tonne of raw waste. The ESP-ash generation rate was calculated to be 11.4 kg from the operational record of the ESP ash stabilizer, which was not operated during the sample collection period. The amount of effluent obtained from the wet scrubber was 0.32 m³ when operated.

The N-incinerator (Fig. 2) had a bag-house filter, a catalytic nitrogen oxide removal device, and a wet scrubber. At the bag-house inlet, 20 kg of lime, on average, was injected. The amount of fly ash was calculated to be 9.8 kg. This is the product of the dust concentration in the flue gas before the bag-house (1.90 g/Nm³, dry) and the flow rate (5180 Nm³, dry). Thus, the amount of bag-house ash was estimated to be 29.8 kg. The amount of effluent obtained from the wet scrubber was 0.11 m³ when operated.

Sample collection

Sample collections were performed in triplicate during November 1995 to March 1996. From the T-incinerator, a mixture of ESP ash and bottom ash (sample A), ESP ash (sample B), and effluent from the wet scrubber (sample C) were collected. Sample A was taken from the ash reservoir, and then dried and sieved (5-mm screen). The material that passed through the sieve was further ground to pass a 1-mm

Table 1. Results of sieve analysis, T-incinerator

	Run 1	Run 2	Run 3	Average	
				$\bar{X} \pm$	σn
Fine particles (%)	19.7	33.7	21.9	25.1 ±	6.1
Bulky fraction (%)	41.4	44.7	60.8	49.0 ±	8.5
Moisture (%)	38.9	21.6	17.3	25.9 ±	9.3

Samples were taken from the ash reservoir

screen. Table 1 shows the measured amounts of moisture, fine particles, and bulky fraction. From the N-incinerator, bottom ash (sample D), bag-house ash (sample E), and effluent from the wet scrubber (sample F) were collected. The results of drying-sieving measurements on sample D are given in Table 2.

Analysis

The analytical protocol is described in elsewhere.⁵ In brief, the arsenic and antimony in the ash were extracted by heated hydrochloric acid-nitric acid. The extract was

Table 2. Results of sieve analysis, N-incinerator

	Run 4	Run 5	Run 6	Average	
				$X \pm$	σn
Fine particles (%)	32.5	28.4	24.8	28.6 \pm	3.1
Bulky fraction (%)	36.0	44.9	43.2	41.3 \pm	3.9
Moisture (%)	31.5	26.7	32.0	30.1 \pm	2.4

Samples were taken from the conveyer at the bottom ash quenching tank

analyzed by batch hydride generation atomic absorption spectrometry.

Results and discussion

Ash production

To estimate the ash production in the T-incinerator, the following the mass balance equation was used:

$$\text{Total ash input} = M_{T(1)} + M_{T(2)} + M_{T(3)} \quad (1)$$

where the total ash input is the ash contained in raw waste (= 164.0 kg), $M_{T(1)}$ is the amount of bulky fraction in the bottom ash (kg), $M_{T(2)}$ is the amount of fine particles in bottom ash (kg), and $M_{T(3)}$ is the amount of ESP ash (=11.4 kg).

The sieve analysis results (see Table 1) gave the following estimation:

$$\{M_{T(3)} + M_{T(2)}\}/M_{T(1)} = 25.1/49.0 \quad (2)$$

For the N-incinerator, the following two equations were used in a similar way:

$$\text{Total ash input} + \text{Lime injection} = M_{N(1)} + M_{N(2)} + M_{N(3)} \quad (3)$$

$$M_{N(2)}/M_{N(1)} = 28.6/41.3 \quad (4)$$

where the total ash input is the ash contained in raw waste (= 164.0 kg), lime injection is the amount of lime injected (= 20.0 kg), $M_{N(1)}$ is the amount of bulky fraction in the bottom ash (kg), and $M_{N(2)}$ is the amount of fine particles in the bottom ash (kg), and $M_{N(3)}$ is the amount of bag-house ash (= 29.8 kg).

Thence, the quantitative mass balance estimations were made (Figs. 1 and 2).

Elemental balance

Arsenic

The elemental balance estimate is given in Table 3 (T-incinerator) and Table 4 (N-incinerator). The following observations were made. (1) The total arsenic in raw waste was 0.89–0.93 g/t; (2) 45–47% of the arsenic was distributed to fly ash; (3) the arsenic captured in the wet scrubber was 0.7% in the incinerator equipped with ESP, and less than 0.05% in the incinerator with the bag-house.

Antimony

From Tables 3 and 4, the following estimation can be made in the same way as for arsenic. (1) The total antimony in raw waste was 30.0–44.3 g/t; (2) 33–74% of the antimony was distributed to fly ash; (3) antimony captured in the wet scrubber was 1.3% in the incinerator equipped with ESP, and less than 0.005% in the incinerator with the bag-house.

Occurrence

Arsenic

Arsenic concentrations in ash were almost constant, although the levels were low. This may suggest that arsenic occurrence in raw waste is widely spread, i.e., it is difficult to distinguish any one particular arsenic source.

Occurrence of arsenic is summarized in Table 5 and compared with earlier reports.^{2,7–13} The concentration of arsenic in fly ash was similar to reports from Spain in 1992² and France in 1998,⁷ but were markedly lower than values from America in 1996⁸ and Canada in 1995.⁹ The total arsenic in raw waste in the present study (0.9 g/t) is lower than that in a similar study conducted by Rigo et al.¹³ in Canada in 1991, in which 7.83 g/t on average was reported. In Japan today, industrial arsenic production is very low. On the other hand, the natural arsenic level in soil in Japan is around 10 mg/kg.¹⁴ Therefore, arsenic occurring in municipal waste incinerators at the level found in this study could be attributed mainly to natural background levels.

Antimony

The occurrence of antimony is summarized in Table 5 and compared with earlier studies.^{2,7–13} Antimony levels obtained here showed good agreement with our previous examination of waste samples.⁴ Moreover, they unexpectedly agreed with the data reported by Rigo et al.¹³ (33 g/t on average) and by Law and Gordon¹² (40 g/t dry, in America in 1979).

Antimony levels in municipal waste are far higher than those in the natural background, e.g., 0.4 mg/kg in soil.¹⁴ In addition, Greenberg et al.¹⁵ and Mamuro et al.¹⁶ have argued that atmospheric antimony is due to emissions from municipal waste incineration. The data fluctuation observed in this study (see Tables 3 and 4) suggested the ubiquity of antimony, which has also been found in waste sample surveys.^{4,10}

Distribution to bottom ash and fly ash

Arsenic

The results obtained suggested that about 50% of arsenic is distributed to fly ash and the rest remains in bottom ash. Distribution to fly ash must involve some volatilization of

Table 3. Balance of arsenic and antimony in the T-incinerator

	ESP ash (Sample B)			ESP ash + bottom ash (Sample A)			Bottom ash			Wet scrubber (Sample C)			Total	
	Concentration (mg/kg)	Ash (kg)	Element (g)	Concentration (mg/kg)	Ash (kg)	Element (g)	Concentration (mg/L)	Effluent (L)	Element (g)	Concentration (mg/L)	Effluent (L)	Element (g)	Element (g)	
As	Run 1	40.8		15.5			0.0035							
	Run 2	36.7		10.3			0.0341							
	Run 3	28.2		21.9			0.0141							
	Average	35.2 ± 5.2	11.4	0.40 (45%)	15.9 ± 4.7	55.6	0.88	0.017 ± 0.013	320	0.006 (0.7%)			0.89 (100%)	
Sb	Run 1	3276		889			0.89							
	Run 2	1117		448			1.01							
	Run 3	1428		262			1.86							
	Average	1940 ± 953	11.4	22.1 (74%)	533 ± 263	55.6	29.6	1.25 ± 0.43	320	0.40 (1.3%)			30.0 (100%)	

ESP, electrostatic precipitator

Table 4. Balance of arsenic and antimony in the N-incinerator

	Bag-house ash (Sample E)			Bottom ash (Sample D)			Wet scrubber (Sample F)			Total		
	Concentration (mg/kg)	Ash (kg)	Element (g)	Concentration (mg/kg)	Ash (kg)	Element (g)	Concentration (mg/L)	Effluent (L)	Element (g)	Element (g)		
As	Run 4	20.4		4.0			<0.001					
	Run 5	18.4		6.6			<0.001					
	Run 6	5.7		12.8			<0.001					
	Average	14.8 ± 6.5	29.8	0.44 (47%)	7.8 ± 3.7	63.1	0.49 (53%)		110	0.000 (0.0%)		0.93 (100%)
Sb	Run 4	734		1007			0.049					
	Run 5	614		85			0.011					
	Run 6	113		325			0.004					
	Average	487 ± 269	29.8	14.5 (33%)	472 ± 391	63.1	29.8 (67%)	0.021 ± 0.020	110	0.002 (0.0%)		44.3 (100%)

Table 5. Summary of reports of arsenic and antimony occurrence in municipal waste incineration

	Arsenic	Antimony	Remark	Ref.
Concentration in fly ash (mg/kg)	25	240	ESP ash, production rate 12 kg/t, Spain 1992	2
	28	720	ESP ash, France 1998	7
	319	1590	ESP ash, America 1996	8
	960	2073	ESP ash, Canada 1995	9
	–	173	ESP ash, production rate 35 kg/t, Japan 1996	10
	–	454	ESP ash, production rate 15.6 kg/t, Japan 1996	10
	30	–	Typical value for ESP ash from incinerators equipped with a boiler, Japan 1995	11
		35	1940	ESP ash, production rate 11.4 kg/t, present study
Distribution to ESP ash (%)	–	45–64	Japan 1996	10
	–	70	America 1979	12
	45–47	33–74	Present study	
Content in raw waste (g/t)	–	10–16	Japan 1996	10
	–	45	Dry base, America 1979	12
	7.8	33	Canada 1991	13
	0.89–0.93	30–44	Present study	

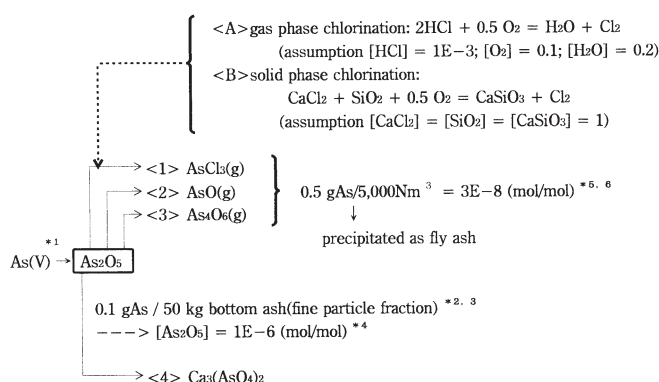


Fig. 3. Fate model of arsenic in an incinerator. *1 Arsenic input has a valency of five (assumption). *2 0.1 g As remains in the fine particle fraction of the bottom ash (assumption). *3 The bottom ash (fine particle fraction) is 50 kg per tonne of raw waste (from the present study). *4 The average molecular weight of the bottom ash is 100 g/mol (assumption). *5 Arsenic precipitated as fly ash is 0.5 g As per tonne of raw waste (from the present study). *6 The volume of the exhaust gas is 5000 Nm³ per tonne of raw waste (from the present study)

arsenic, although, the form of the arsenic is subject to debate. As₄O₆ has been considered to be the most stable form, even in the presence of 10% chlorine in the feed fuel.¹⁷ On the other hand, Wu and Biswas¹⁸ have stated that the affinity of arsenic to chlorine is greater than mercury and cadmium, but smaller than lead. It is interesting to postulate an arsenic fate model in which chloride and oxide formation are in competition, assuming the typical conditions of an actual incinerator.

This fate model is shown in Fig. 3. The initial valency of arsenic is thought to be five, because As(V) is more stable than As(III) in air,¹⁹ and As(III) should not be added to household materials because of its toxicity. In the following discussion, all values are stated per tonne raw waste. It is assumed that 0.1 g of As remains in the fine bottom ash (50

kg) as As₂O₅. Possible transformations from As₂O₅ are to <1> As₄O₆ (g), <2> AsO (g), <3> AsCl₃ (g), and <4> Ca₃(AsO₄)₂. The activity of As₂O₅ in bottom ash was calculated to be 1 × 10⁻⁶, assuming the average molecular weight of fine bottom ash to be 100 (g/mol). Atmospheric conditions are assumed to be [O₂] = 0.1, [H₂O] = 0.2, and [HCl] = 1 × 10⁻³. Arsenic can be chlorinated through a gas-phase reaction <A>:



As well as <A>, a solid-phase reaction involving calcium–silica is also taken into account.



From the field study, arsenic from the precipitator was 0.5 g As, which gives 3 × 10⁻⁸ (mol/mol) of arsenic concentration in the gas phase, considering a gas volume of 5000 Nm³. That is the required concentration of arsenic which must be volatilized to allow the transport of 0.5 g As per tonne from the bottom ash.

All equilibrium coefficients (K_p) were taken from the thermodynamics database MALT 2.²⁰ The equations, K_p, assumed conditions, and results are given in Table 6. The predicted activities of arsenic compounds in equilibrium as [As₂O₅] = 1 × 10⁻⁶ in the solid phase are shown in Fig. 4. The dominant compound was Ca₃(AsO₄)₂, which suggested a strong potential to confine arsenic to the bottom ash. This could explain the phenomena observed by Waterland et al.¹

Among gas-phase compounds, AsCl₃ (g) through predominated over other compounds, including AsCl₃ (g) through <A>. Furthermore, only AsCl₃ (g) through exceeded 3 × 10⁻⁸ (mol/mol), in other words, it could transport sufficient arsenic to the fly ash.

However, the possibility of oxide formation still remains. AsO (g) or As₄O₆ (g) might occur to a considerable degree at high temperatures, because As₂O₅ is degraded at T = 799°C, giving oxide gas. Nevertheless, it would not occur

Table 6. Thermodynamic calculation on arsenic and antimony using the fate models

								Temp. (°C)	300	400	500	600	700
<A>	2 HCl	+ 0.5 O ₂	= 1 H ₂ O	+ 1 Cl ₂				Kp	6.5E+01	1.1E+01	2.8E+00	9.7E-01	4.2E-01
Assumed value	0.001	0.1	0.2					[Cl ₂]eq	1.0E-04	1.7E-05	4.4E-06	1.5E-06	6.6E-07
	1 CaCl ₂	+ 1 SiO ₂	= 0.5 O ₂	+ 1 CaSiO ₃				Kp	3.9E-04	2.8E-03	1.2E-02	3.6E-02	8.5E-02
Assumed value	I	I	0.1	I				[Cl ₂]eq	1.2E-04	8.9E-04	3.8E-03	1.1E-02	2.7E-02
<1-A, B>	0.5 As ₂ O ₅	+ 1.5 Cl ₂	= 1 AsCl ₃	+ 1.25 O ₂				Kp	8.0E-09	3.6E-06	3.1E-04	8.8E-03	1.2E-01
Assumed value	1.0 × 10 ⁻⁶	from [A]		0.1				[AsCl ₃]eq	8.3E-18	2.6E-16	2.9E-15	1.7E-14	6.5E-14
Assumed value	1.0 × 10 ⁻⁶	from [B]		0.1				[AsCl ₃]eq	1.1E-17	9.5E-14	7.2E-11	1.1E-08	5.3E-07
<2>	0.5 As ₂ O ₅	+ 1 AsO	= 1 AsO	+ 0.75 O ₂				Kp	4.8E-32	6.4E-25	1.1E-19	1.1E-15	1.5E-12
Assumed value	1.0 × 10 ⁻⁶			0.1				[AsO]eq	2.7E-34	3.6E-27	6.2E-22	6.2E-18	8.4E-15
<3>	2 As ₂ O ₅	+ 2 O ₂	= 1 As ₄ O ₆	+ 2 O ₂				Kp	6.1E-29	1.7E-20	2.2E-14	8.5E-10	2.7E-06
Assumed value	1.0 × 10 ⁻⁶			0.1				[As ₄ O ₆]eq	6.1E-39	1.7E-30	2.2E-24	8.5E-20	2.7E-16
<4>	1 As ₂ O ₅	+ 3 CaO	= Ca ₃ (AsO ₄) ₂					Kp	-	2.0E+36	3.1E+31	5.3E+27	4.7E+24
Assumed value	1.0 × 10 ⁻⁶	I						[Ca ₃ (AsO ₄) ₂]eq	-	2.0E+30	3.1E+25	5.3E+21	4.7E+18
<5-A, B>	0.25 Sb ₄ O ₆	+ 1.5 Cl ₂	= 1 SbCl ₃	+ 0.75 O ₂				Kp	1.8E+01	5.9E+01	1.4E+02	2.8E+02	3.9E+02
Assumed value	1.7 × 10 ⁻⁵	from [A]		0.1				[SbCl ₃]eq	6.8E-06	1.5E-06	4.7E-07	1.9E-07	7.6E-08
Assumed value	1.7 × 10 ⁻⁵	from [B]		0.1				[SbCl ₃]eq	8.9E-06	5.6E-04	1.2E-02	1.2E-01	6.2E-01
<6>	0.25 Sb ₄ O ₆	+ 1 SbO	= 1 SbO	+ 0.25 O ₂				Kp	-	5.8E-32	1.9E-26	3.2E-22	6.1E-19
Assumed value	1.7 × 10 ⁻⁵			0.1				[SbO]eq	-	6.6E-33	2.2E-27	3.7E-23	7.0E-20
<7>	1 Sb ₄ O ₆	+ 1 Sb ₄ O ₆	= 1 Sb ₄ O ₆					Kp	6.2E-09	2.9E-06	2.6E-04	8.3E-03	6.5E-02
Assumed value	1.7 × 10 ⁻⁵							[Sb ₄ O ₆]eq	1.0E-33	2.9E-25	3.7E-19	1.4E-14	4.6E-11
<8-A, B>	0.5 Sb ₂ O ₄	+ 1.5 Cl ₂	= 1 SbCl ₃	+ 1 O ₂				Kp	5.9E-06	4.4E-04	1.0E-02	1.2E-01	8.1E-01
Assumed value	3.3 × 10 ⁻⁵	from [A]		0.1				[SbCl ₃]eq	3.5E-13	1.8E-12	5.4E-12	1.3E-11	2.5E-11
Assumed value	3.3 × 10 ⁻⁵	from [B]		0.1				[SbCl ₃]eq	4.6E-13	6.7E-10	5.9E-09	8.4E-06	2.1E-04
<9>	0.5 Sb ₂ O ₄	+ 1 SbO	= 1 SbO	+ 0.5 O ₂				Kp	-	4.3E-37	1.4E-30	1.0E-25	1.3E-21
Assumed value	3.3 × 10 ⁻⁵			0.1				[SbO]eq	-	7.8E-39	2.5E-32	1.8E-27	2.4E-23
<10>	2 Sb ₂ O ₄	+ 1 Sb ₄ O ₆	= 1 Sb ₄ O ₆	+ 1 O ₂				Kp	7.7E-35	8.5E-27	7.6E-21	2.9E-16	1.3E-12
Assumed value	3.3 × 10 ⁻⁵			0.1				[Sb ₄ O ₆]eq	8.4E-43	9.3E-35	8.3E-29	3.2E-24	1.4E-20

predominantly in a municipal waste incinerator, because some confining reaction with the ash matrix, such as $\text{Ca}_3(\text{AsO}_4)_2$ formation, should already be finished before the included arsenic is heated to 800°C .

A general overview of the behavior of arsenic is given in Fig. 5. Note that if the included arsenic were in the form of As_4O_6 or AsCl_3 , all of the arsenic would be volatilized. Thus, the actual distribution depends on the initial valency.

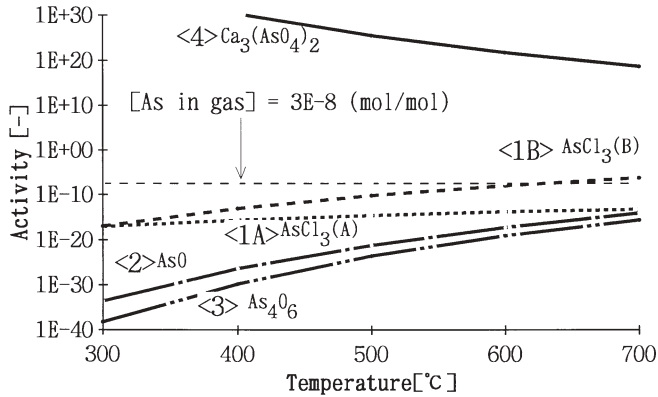
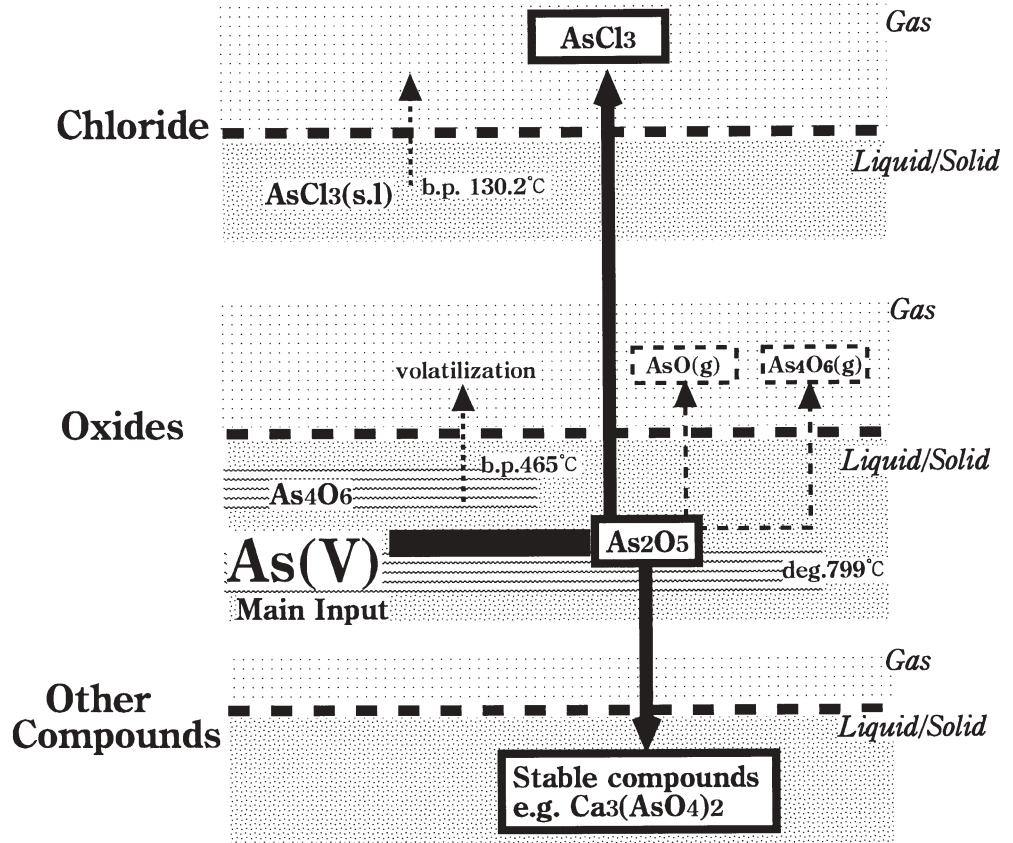


Fig. 4. Predicted activities of arsenic compounds in equilibrium with As_2O_5 in bottom ash

Fig. 5. Behavior of arsenic in a municipal waste incinerator



Antimony

Antimony volatilization can be examined in a similar way to that of arsenic. However, the initial valency of included antimony was thought to be mainly three, because the compound Sb_4O_6 is widely used. However, Sb_2O_4 is more stable than Sb_4O_6 up to 900°C . Hence, we propose the antimony fate model shown in Fig. 6. Included antimony has a valency of three, which can transform to <5> SbCl_3 (g), <6> SbO (g), <7> Sb_4O_6 (g), Sb_2O_4 , and stable compounds with a matrix. The Sb_2O_4 formed can produce <8> SbCl_3 (g), <9> SbO (g); <10> Sb_4O_6 (g), and stable compounds with a matrix. Unfortunately, no equilibrium coefficient was obtained for antimony–ash matrix compounds, although some such reactions should occur. Two possible chlorinating reactions, <A> and , are in operation. The amounts of antimony in bottom ash as Sb_2O_4 and Sb_4O_6 are assumed to be 5 g in each. The required antimony volatilized from the bottom ash is 15 g, giving 6×10^{-7} (mol/mol) in the gas phase.

The calculation and results are given in Table 6. Figure 7a,b shows the virtual activities of antimony compounds from Sb_4O_6 and Sb_2O_4 , respectively. SbCl_3 (g) from Sb_4O_6 through could considerably exceed the activity required to bring 15 g Sb to fly ash. SbCl_3 (g) from Sb_4O_6 through <A> and SbCl_3 from Sb_2O_4 through could provide the gas-phase antimony equivalent required. In both cases, volatilization as oxide hardly occurred.

Fig. 6. Fate model of antimony in an incinerator. *1 Antimony input has a valency of three (assumption). *2 The fine bottom ash involves Sb_4O_6 (5 g Sb) and Sb_2O_4 (5 g Sb) (assumption). *3 Antimony precipitated as fly ash was 15 g Sb per tonne of raw waste (from the present study)

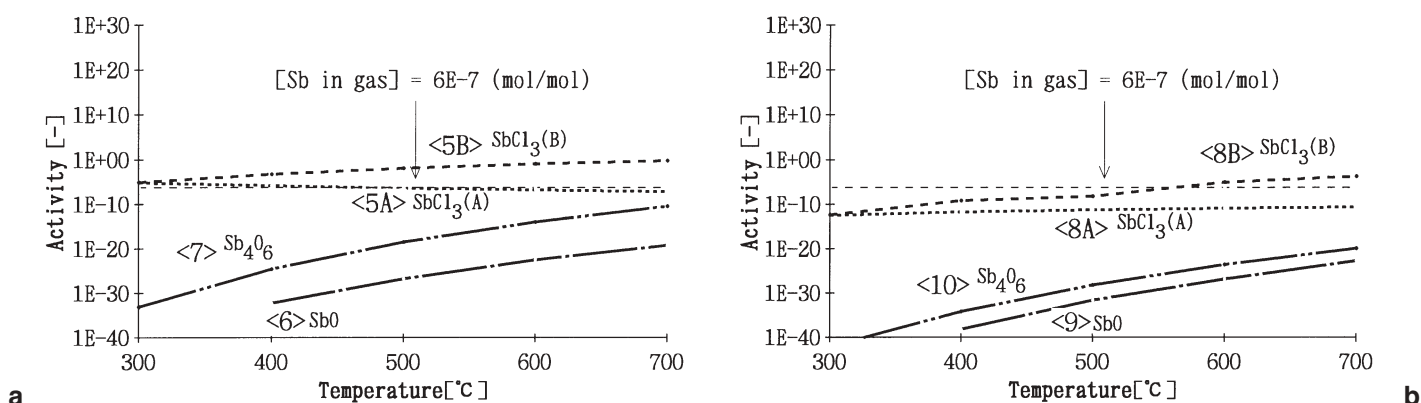
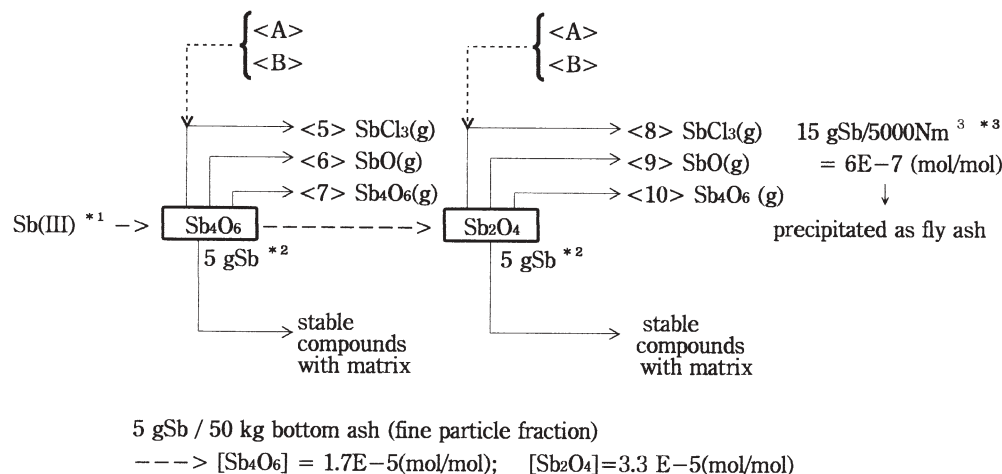


Fig. 7. Predicted activities of antimony compounds in the fate model. **a** In equilibrium with Sb_4O_6 in bottom ash. **b** In equilibrium with Sb_2O_4 in bottom ash

A general overview of the behavior of antimony is shown in Fig. 8. Antimony volatilization was due to chlorination rather than volatile oxide formation. In a laboratory experiment, we also observed that waste heated at 500°C resulted in 50% antimony volatilization, while only 10% of heated Sb_4O_6 was volatilized at 500°C .²¹ This experiment also provided evidence of a solid-phase chlorine reaction . The extremely high activity of SbCl_3 (g) from Sb_4O_6 through could explain the scattered data of antimony concentrations in ESP ash, as well as the ubiquity of antimony in waste.

Conclusion

Arsenic and antimony balances in real municipal waste incinerators were investigated. The total amounts of arsenic and antimony in municipal waste were 0.9 g/t and 30–44 g/t, respectively. The occurrence of arsenic in municipal waste was considered to be as low as the natural background level, while the antimony concentration level was rather higher.

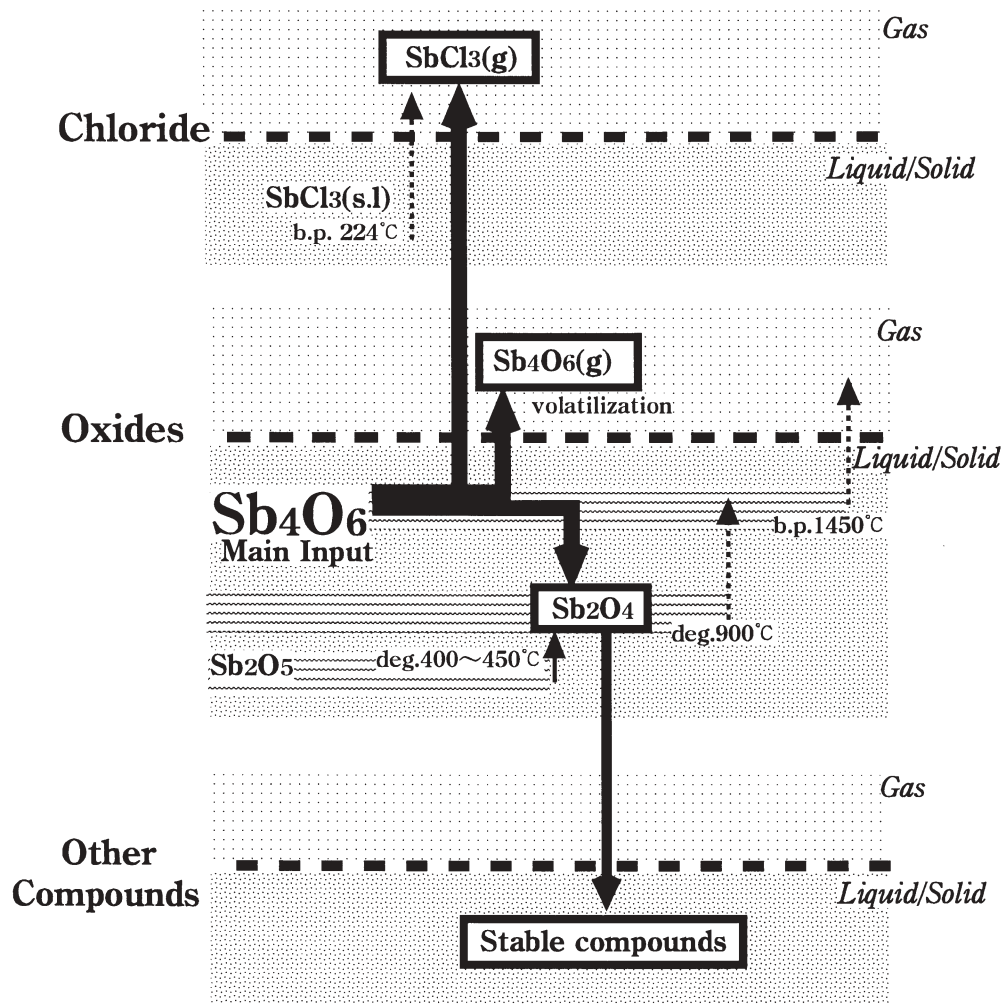
The distributions in fly ash were 45–47% and 33–74% for arsenic and antimony, respectively.

The distribution mechanism of arsenic was considered to be as follows. Most of the arsenic entering the system was thought to have a valency of five, giving As_2O_5 , from which some volatilization should occur. A thermodynamic examination of the competition between volatile chloride formation and volatilization as oxide revealed chlorinated arsenic to be predominant. At the same time, some reaction with the ash matrix, for example, $\text{Ca}_3(\text{AsO}_4)_2$ formation, to confine the arsenic in bottom ash would occur.

The distribution mechanism of antimony was considered to be as follows. Most of the antimony entering was thought to have a valency of three, giving Sb_4O_6 , from which Sb_2O_4 would be formed. Chloride formation from Sb_4O_6 could be very intensive, while that from Sb_2O_4 was as moderate as the arsenic chloride formation from As_2O_5 . Volatilization as oxide would hardly occur.

When considering chloride formation of both arsenic and antimony in municipal waste incineration, not only the

Fig. 8. Behaviour of antimony in a municipal waste incinerator



gas-phase reaction, but also the solid-phase reaction should be taken into account.

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