

Experimental and thermodynamic investigation on transfer of cadmium influenced by sulfur and chlorine during municipal solid waste (MSW) incineration

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Abstract

We used two approaches to investigate the impact of sulfur and chlorine compounds on transfer of a semivolatile heavy metal, cadmium, during municipal solid waste (MSW) incineration: experiments using a tubular furnace reactor and thermodynamic equilibrium calculations. Artificial wastes representative of typical MSW in China with and without the presence of sulfur and chlorine compounds were combusted at 850 °C, and the partitioning of Cd among bottom ash, fly ash and flue gas was quantified. The results indicate that sulfur compounds in the elemental form and reduced state could stabilize Cd in the form of CdS due to local reducing environment, while sulfur in the oxidized forms slightly increased Cd volatilization during incineration. In contrast, the presence of chlorine compounds significantly increased the partitioning of Cd on fly ash. Chemical equilibrium calculations show that sulfur binds with Cd and alters Cd speciation at low temperatures (<700 °C), while chlorine significantly increases the volatilization of Cd through formation of volatile CdCl₂ and thus its partitioning on the fly ash between 400 and 1000 °C. The equilibrium calculation results also suggest that SiO₂- and Al₂O₃-containing minerals could function as sorbents stabilizing Cd as condensed phase solids (CdSiO₃ and CdAl₂O₄). These findings provide useful information on understanding the partitioning behavior of Cd and can help development of strategies to control volatilization of Cd during MSW incineration.

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1. Introduction

Waste incineration plants transform heterogeneous wastes into more homogeneous residues (flue gas, fly ash and bottom ash). Municipal solid waste (MSW) incineration presents two advantages: reduction of the waste volume (by 90%) and destruction of organic compounds (near complete), bacteria and viruses. On the other hand, the metal species contained in the waste are not destroyed during high-temperature incineration, but instead condense to form metallic particles during the cooling of the flue gas. Heavy metals may be concentrated in the solid residues (bottom ash and fly ash) of MSW incinerators, or as airborne aerosols exiting the stack. Different heavy met-

als exhibit significantly different partitioning behaviors during incineration: Fe and Cu are almost entirely trapped in the bottom ash, Hg and even Cd are almost totally in the flue gas, while Pb, Zn and As are nearly distributed to 1/3 in fly ash and 2/3 in bottom ash [1–3]. The emissions of heavy metals from MSW incineration are hazardous to human health and the surrounding environment [4,5].

Upon entry to the combustion chamber, semivolatile elements such as lead and cadmium vaporize in the high-temperature region within the incineration systems. As the process temperature decreases, these metals begin to condense following several mechanisms [6]. A small fraction of the metal is partitioned to small submicron particles, and the resulting particulate matter is often highly enriched in the semivolatile metals. The remaining metal condenses to larger fly ash particles, which are easily separated and contained within the process. In contrast, the fine (submicron) particulates can penetrate conventional air

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pollution control systems, such as wet scrubbers, baghouses and electrostatic precipitators, and be emitted to the atmosphere [6]. These particulates may contact human populations directly through inhalation, drinking water contamination (deposition on lakes and rivers), and indirectly through the food chain [5].

Cadmium is one of the most harmful heavy metals emitted from MSW incinerators. It can be present in the waste input to an incinerator in the form of the metal (e.g., as cadmium plating), salts (e.g., CdCl_2 , CdSO_4 and CdS) and alloys (e.g., some solders and batteries). Cadmium and its salts can be vaporized during waste incineration and emitted to the atmosphere as elemental cadmium, chlorides or oxides. Such vapors rapidly condense onto particle surfaces, either those emitted simultaneously or ambient particles, and the fine-particle fractions become relatively enriched in cadmium because of their higher surface area per unit mass [7]. Most of the cadmium that occurs in air is associated with particulate matter in the respirable range (0.1–1 μm diameter), and its residence time is relatively short (days to weeks) but sufficient to allow long-range transport in the atmosphere [7]. Cadmium is recognized as a potential human carcinogen [8], and the State Environmental Protection Administration of China has set its emission standard from MSW incinerators at 0.1 mg/m^3 [9].

Partitioning of heavy metals among the various incinerator residues depends on the MSW composition, the physicochemical properties of the metals and their compounds, and the incinerator operating conditions [10–13]. To understand the transfer of heavy metals during MSW incineration, it is necessary to study the influence of combustion conditions, such as temperature, gas composition, residence time and the presence of reactive compounds (chlorine, sulfur, or aluminosilicates), on the final metal speciation in the residues [1].

MSW is a heterogeneous material and its production rate and physical composition vary from place to place as they are a function of socio-economic level and climatic conditions [14]. In China, the physical components of MSW typically include food waste, paper, plastics, glass, metals, textiles, rubber, wood and inert materials (stones, ceramics, ashes, etc.). Small amounts of industrial wastes and construction wastes may also end up in MSW some times. Waste sorting is not implemented in China and these components are not separated. On the other hand, some of the MSW components, such as metals and paper, are highly recycled due to their values. Because of the life style differences and the current trash disposal practice, MSW in China shows some distinct compositional characteristics. Table 1 compares the average compositions of MSW in selected cities in China with those in other developing and developed countries. It can be seen that food waste makes up the largest fraction (approximately 50%) of MSW in China, like in other developing countries. In contrast, paper makes up the largest component of MSW generated in the developed countries (Italy and U.S.). In the incineration of unsorted MSW, chlorides from PVC (polyvinyl chloride) plastic, food residues, and various other sources can significantly enhance metal volatilization through the formation of metal chlorides, increasing toxic heavy metal emissions [1,15].

Table 1
Comparison of the characteristics of MSW generated in selected cities in China with those of MSW from other countries

City/country	Year	Food waste (wt.%)	Inert matter (wt.%)	Paper (wt.%)	Textile, rubber and leather (wt.%)	Wood and yard trimming (wt.%)	Plastic (wt.%)	Glass (wt.%)	Metal (wt.%)	Water (wt.%)	Calorific value (kcal/kg)
Changzhou ^a	1997	44.4	34.6	3.6	3.2	1.8	8.0	3.50	1.0	48.5	716
Hangzhou ^a	1997	58.2	24.0	3.7	3.2	1.2	6.6	2.1	1.0	53.6	1060
Wenzhou ^a	1998	44.7	17.9	7.7	1.7	1.9	23.9	1.3	1.0	52.0	1600
Guangzhou ^a	1996	60.2	17.1	5.4	3.4	1.1	9.0	3.4	0.5	50.1	1050
Shenzhen ^a	1994	40.0	15.0	17.0	7.0	–	13.0	5.0	3.0	45.0	1347
Changchun ^a	2000	75.7	10.0	6.1	1.3	–	2.2	1.0	0.3	51.0	1007
Qinhuangdao ^a	2003	43.4	37.7	6.8	3.9	0.9	4.3	2.7	0.3	44.6	980
Kuala Lumpur, Malaysia ^b	2000	51.9	2.2	11.2	2.3	6.3	21.0	2.5	2.5	55.0	2400–4000
Jordan ^c	1995	62.6	5.6	11.4	–	–	16.2	2.1	2.1	60.1	2750
Parona, Italy ^d	2006	20	11.0	29.5	3.5	11.0	13.5	8.0	3.5	20–30	2500–3970
United States ^e	1997	6.7	3.2	39.2	6.5	21.4	9.1	6.2	7.6	20.0	2000–4200

^a From [38].

^b From [39].

^c From [40].

^d From [41].

^e From [42].

Another distinct character of MSW in developing countries is its high moisture levels (typically around 50%), which is much higher than that (20–30%) in the MSW from U.S. and European countries. Because of the traditions of materials recovery and extensive picking in China, the calorific values in the MSW streams are rather low. The high moisture content further lowers the MSW's energy content. Consequently, the calorific values (700–1600 kcal/kg) of MSW in China are typically less than half of those of the MSW in the developed countries, which are mainly composed of sorted organic wastes. As a result, auxiliary fuel is necessary for MSW incinerators, and coals that typically contain high levels of sulfur are commonly used for this purpose in China because of their low cost [16]. Most heavy metals could form sulfate salts in the presence of sulfur at temperatures below 700 °C [17]. Sulfur present in the coal may interact with heavy metals, such as Cd, during MSW incineration and affect their emissions. Sulfur can, in principle, delay heavy metal volatilization when the incineration temperature is below 800 °C [29]. With the common practice of co-firing of MSW with sulfur-containing coals in China, the impact of sulfur compounds on heavy metal partitioning during MSW incineration is an important issue to be studied.

The objective of this study was to experimentally quantify the impact of sulfur and chlorine on the partitioning of Cd under simulated MSW incineration conditions and to understand its speciation from thermodynamic calculations. Artificial MSW representative of the wastes generated in Chinese cities was combusted in a tubular furnace reactor, which served as a model of a fixed-bed waste incinerator, and the impact of various sulfur and chlorine compounds on Cd partitioning among bottom ash, fly ash and flue gas was measured. The partitioning of Cd under incineration conditions was thermodynamically predicted in a well-defined system whose composition corresponds to that during the incineration of the artificial MSW. The equilibrium calculations focused on the influences of the operating temperature, and the presence of sulfur and chlorine in the combustion gas on Cd speciation. Theoretical analysis was also conducted to investigate the potential role of SiO₂- and Al₂O₃-containing materials as sorbents for Cd stabilization in fluidized bed incinerators. The results can help to better understand the emission of Cd from MSW incinerators and to develop effective heavy metal control strategies.

2. Experimental

2.1. Materials

Studying the combustion of actual MSW in laboratory scale combustors was difficult because many variables in the experiments were uncontrolled or complicated to measure [18]. The artificial MSW used in this study was developed based on the typical physical components of the MSW from Chinese cities, using the simple chemically defined materials shown in Table 2. In the artificial wastes, flour, corrugated paper, wood chips, cotton cloth, polythene and inert materials (50% SiO₂ + 50% Al₂O₃) were used to simulate the physical components of the wastes, including food residue, paper, wood, textiles, plastic, and noncombustible materials (such as glass, ceramic and sand), respectively. The contents of these components in the artificial MSW prepared are also shown in Table 2. The moisture content was adjusted to 50% to reflect the high moisture content characteristic of the MSW in China. Since the background heavy metal concentrations in the above artificial components were negligible, Cd was added to the synthetic waste in the form of (CH₃COO)₂Cd·2H₂O to the concentration of 200 mg Cd/kg (dry weight). Although the Cd concentration in the artificial MSW studied is much higher than those in typical MSW (5–15 mg Cd/kg), it is comparable or lower to the Cd concentrations spiked in other experimental studies [15,19].

The typical sulfur content of MSW in China is 0.1%, while coals may have sulfur contents up to 4%. Synthetic wastes with sulfur contents in the range of 0.1–1.0% (dry weight) were prepared by adding S, Na₂S, Na₂SO₃ and Na₂SO₄ to the artificial MSW; wastes with 2%, 4% and 8% (dry weight) chlorine were also obtained by adding NaCl and PVC. These compounds with different valency state and bonding types were used to simulate different sulfur and chlorine sources in the wastes.

2.2. Experimental apparatus

The apparatus used in this study was composed of an electric-heated tube furnace and a sampling train of impingers as shown in Fig. 1a. It has been shown that incineration experiments in the tubular furnace reactor with small quantities of synthetic waste and properly maintained conditions could simulate the complex processes in the grate furnace of an MSW incinerator

Table 2
Elementary analysis of the artificial MSW components and their contents

Component in artificial waste	Ultimate analysis (wt.%) (dry basis)					Proximate analysis (wt.%)			Calorific value (kcal/kg)	Content in artificial MSW (%)
	C	H	O	N	S	Moisture	Ash	Volatile		
Flour	43.47	6.74	46.76	2.93	0.10	12.75	0.54	79.04	7460	40
Corrugated paper	39.44	5.60	53.73	1.13	0.10	9.41	7.46	83.55	3810	25
Wood chips	48.04	6.34	44.65	0.97	N/D	42.56	0.57	56.51	4582	10
Polythene	85.34	14.57	0.09	0	N/D	0.09	0.56	99.87	11029	10
Cotton cloth	41.34	6.28	50.88	1.47	0.03	6.73	0.82	92.33	3982	5
Inert materials										10

N/D: not detected.

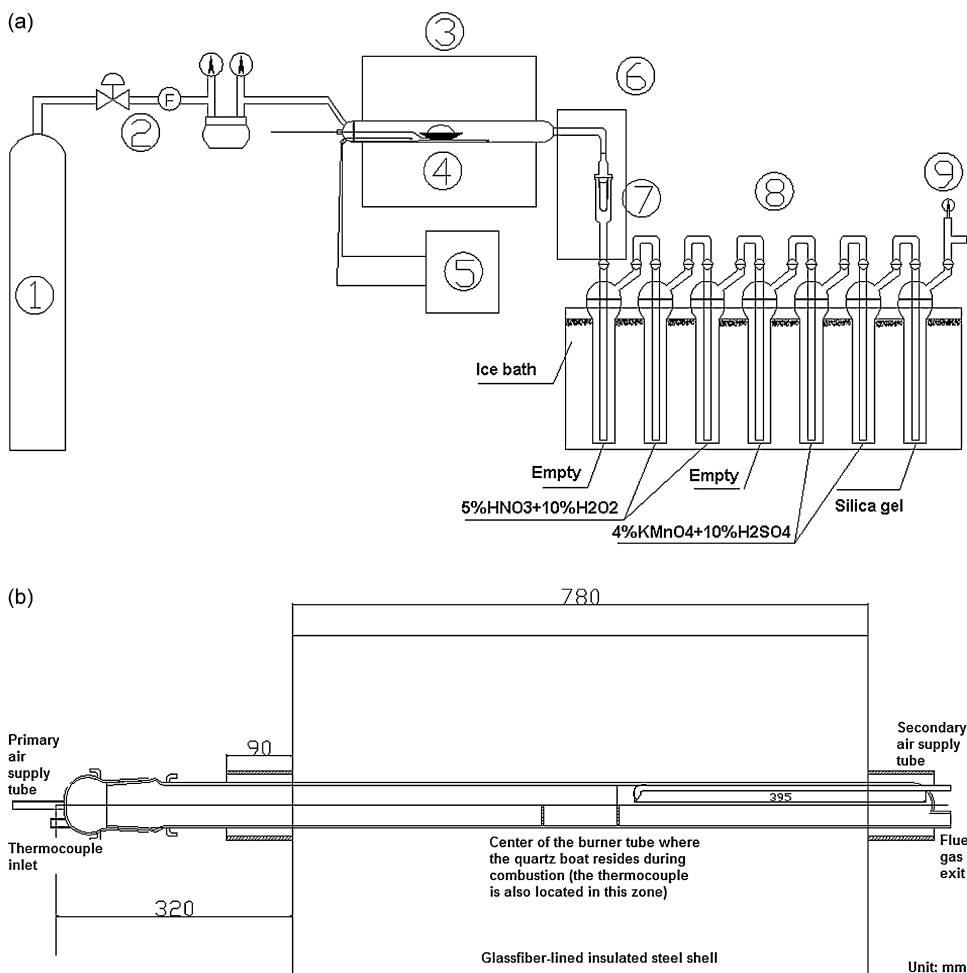


Fig. 1. Schematic diagrams of (a) the laboratory incinerator and the sampling setup and (b) the quartz burner tube, where (1) compressed air cylinder, (2) flow controller, (3) tubular furnace with a quartz burner tube, (4) quartz boat connected with a quartz rod, (5) programmable temperature controller with a thermocouple located in inside the burner tube in the center (measures the flue gas temperature), (6) oven, (7) glass fiber filter, (8) impinger train, and (9) temperature probe.

[20]. A quartz tube burner (Fig. 1b) was housed in a glassfiber-lined insulated steel shell, and a quartz boat moved by a quartz rod was used to feed the synthetic waste into the combustion chamber. The combustion temperature at the center inside the burner tube was monitored by a thermocouple and controlled by a programmable temperature controller. A quartz-fiber filter was set up downstream from the combustion chamber. The temperature of the filter together with its holder was maintained above 120 °C by an oven to prevent the flue gases from condensing while flowing through the filter.

The exhaust gas stream first passed through the 0.3 μm pore size quartz-fiber filter (99.99% effective), then through the impinger train consisted of seven impingers in series immersed in an ice bath for trapping of Cd and its compounds in the combustion gas. The first impinger was empty, the second and third impingers contained 10% H₂O₂ (v/v) and 5% HNO₃ (v/v), the fourth impinger was empty, the fifth and sixth impingers contained acidified potassium permanganate solution (4% KMnO₄ (w/v) and 10% H₂SO₄ (v/v)), and the seventh impinger was filled with silica gel to absorb residual moisture in the flue gas, which were prepared according to the standard method [21].

2.3. Experimental procedure

The effects of combustion time and temperature on Cd partitioning were first determined for the artificial MSW without sulfur or chlorine addition. Five levels of sulfur (0.1–1.0%) and three levels of chlorine (2–8%) were then tested to study their impact of Cd volatilization. Most of the combustion experiments were conducted at 850 °C; the combustion time was kept at 12 min, which was determined from sample weight loss. After the given furnace temperature was reached, the combustion experiment was started by gradually pushing the quartz boat (loaded with the artificial MSW sample) forward into the central part of the combustion chamber in 30 s. The sample loading from the left side opening of the quartz tube to the center simulated the drying/pyrolysis occurring at the beginning of MSW incineration [20]. Combustion air was supplied by a compressed air cylinder at a total flow rate of 11–13 L/min (8–10 L/min from the primary air supply tube and 3 L/min from the secondary air supply tube) at room temperature, under one unit atmospheric pressure. At the end of combustion period, the air supplies were turned off and the quartz boat was pulled out of the quartz tube.

Table 3
The Cd, Si and Al species in the gas and condensed phases considered in the thermodynamic equilibrium simulation

Element	Gas phase species	Condensed phase species
Cd	Cd(g), CdO(g), CdS(g), CdCl ₂ (g)	Cd(l), CdO(s), CdS(s), CdSO ₄ (s), Cd(OH) ₂ (s), CdSiO ₃ (s), CdCO ₃ (s), CdAl ₂ O ₄ , CdCl ₂ (l), CdCl ₂ (s)
Si	Si, Si ₂ , Si ₃ , SiC, SiC ₂ , Si ₂ C, SiH, SiH ₂ , SiH ₃ , SiH ₄ , Si ₂ H ₂ , Si ₂ H ₃ , Si ₂ H ₅ , Si ₂ H ₆ , Si ₃ H ₈ , SiO ₂ , SiO, SiN, Si ₂ N, SiCl, SiCl ₂ , SiCl ₃ , SiCl ₄ , SiS, Si ₂ Cl ₅ , Si ₂ Cl ₆	Si(l), SiO ₂ (l), SiS ₂ (l), Si(s), SiO ₂ (s), SiS ₂ (s), SiC(s), Si ₃ N ₄ (s)
Al	Al, Al ₂ , AlC, AlH, AlH ₂ , AlH ₃ , Al ₂ H ₆ , AlO, AlO ₂ , Al ₂ O, Al ₂ O ₂ , AlN, AlHO ₂ , AlCl, AlCl ₂ , AlCl ₃ , Al ₂ Cl ₆ , AlClO, Al(OH) ₂ Cl, AlOHCl ₂ , AlS	Al(l), Al ₂ O ₃ (l), Al(s), AlN(s), AlCl ₃ (s), AlClO(s), AlOH(s), Al(OH) ₂ (s), Al(OH) ₃ (s), Al(OH) ₂ Cl(s), Al ₂ O ₃ (s), Al ₄ C ₃ (s), Al ₂ S ₃ (s), Al ₂ SiO ₅ (s), Al ₆ Si ₂ O ₃ (s), AlH ₃ (s)

2.4. Analysis methods

At the end of each batch combustion experiment, the residues in the quartz boat were collected as bottom ash; combustion gas samples were taken from the impingers. Total particulate matter (fly ash) was determined from the mass collected on the filter and the material that condensed above the filtration temperature on the connecting tube, following the standard recover procedures [22]. Cd contents of the bottom ash and fly ash and volatile Cd absorbed in the solutions were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), after digestion (if necessary) following the standard procedures [21]. The metal distributions were reproducible to within 3.5% based on results of six replicate experiments. Morphological characteristics of selected bottom ash samples were also examined under a scanning electron microscope (SEM) and qualitative elemental analysis was conducted using the energy dispersive X-ray spectroscopy (EDS) technique.

3. Thermodynamic equilibrium simulation

Chemical equilibrium calculations were carried out to predict the tendency of Cd evolution under various incineration conditions. Thermodynamic equilibrium simulation principally delineates the stable phases that can form under specific operating conditions. When both analytical and thermodynamic data are assimilated, the reaction mechanisms and pathways of trace elements in the incineration process may be proposed [23]. When burning, MSW constitutes a multi-component and multi-phase system. At equilibrium the free energy of a system is minimized. By combining this fact with mass conservation constraints it is possible to develop a series of algebraic equations that can be solved to determine the equilibrium composition of a given system [23].

The method of element chemical potentials combined with atom population constraints was operated on CHEMKIN software [1,24]. The thermodynamic data for all species except those of Cd, such as heat capacity, entropy and enthalpy, were from CHEMKIN data files (therm.dat and janaf_therm.dat) and other thermochemical databases [25,26]. The thermodynamic data of Cd species were obtained from Knacke et al. [27] and converted into CHEMKIN-compatible fitting coefficients using the included FITDAT routine. The system was set up to represent the burning of the artificial MSW in a combustion atmosphere whose composition is similar to that in the burner tube. The

solid wastes used in the model simulation were assumed to consist of the major elements C, H, N, O, and S, as shown in Table 2. The overall Cd content considered was 200 mg Cd/kg (dry weight). Equilibrium calculations were performed in the range 400–1800 K (127–1527 °C), and the total pressure was 1 atm. The air excess ratio was at 1.5 for all calculations, which is typical for MSW burning [1]. The air was assumed to be composed (mole fractions) of 78.5% N₂, 20.5% O₂ and 1% H₂O.

A total of eight elements (C, H, O, N, S, Cl, Cd, Si and Al) were considered in the equilibrium calculations. Besides the gas phase species (H₂, HO₂, O, OH, H₂O, H₂O₂, C, CO, CO₂, N, N₂, NO, NO₂, S, SO₂ and SO₃) of C, H, O, N and S, the Cd, Si and Al species in the gas and condensed phases derived from these elements, which are shown in Table 3, were also considered. The final equilibrium state was obtained by determining all possible species that could be derived from the elements of the input system. The thermodynamic analysis serves to determine the major Cd species and the volatilization tendencies under specific incineration conditions, and to predict the possible chemical interactions between Cd and the matrix components.

4. Results and discussion

4.1. Impact of incineration time and temperature

Fig. 2a shows the weight loss of the artificial MSW as a function of incineration time, calculated from the weight differences of the initial waste and the bottom ash before and after incineration. For all experiments, combustion of the MSW was typically observed to start at around 30 s (right after being loaded to the center of the burner tube). The weight loss occurred rapidly within the first 2 min of incineration, while little change in the mass of bottom ash occurred after that. Water flash vaporization and the quick release of volatile components at 850 °C were responsible for most of the initial weight loss. The most important reaction in MSW incineration is the combustion of carbon and its compounds to CO₂. The fact that the weight of the bottom ash remained essentially constant from 5 to 20 min of incineration indicates the artificial MSW was easy to combust and combustion occurred quickly.

Fig. 2b shows Cd portioning among the bottom ash, fly ash and flue gas as a function of incineration time. The fraction of Cd in the fly ash increased gradually with incineration time, while essentially no Cd was found in the flue gas. The release of

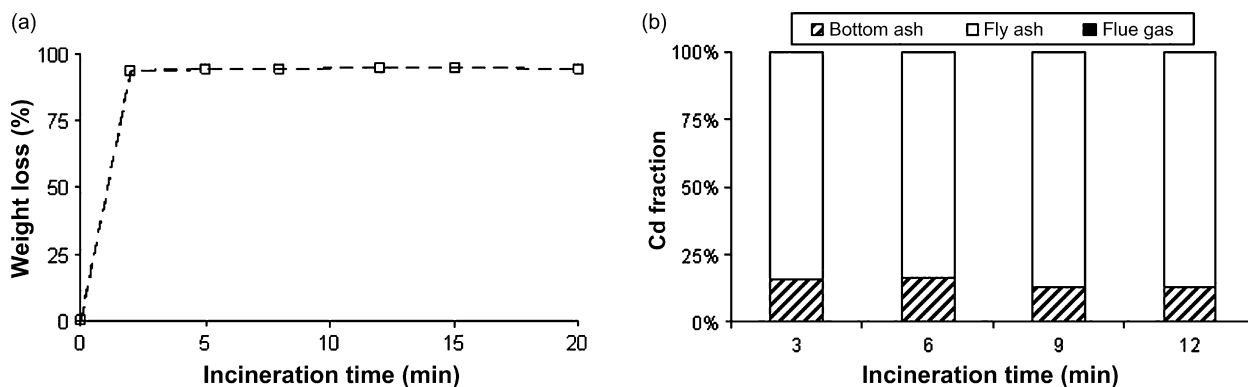


Fig. 2. Effect of incineration time (at 850 °C) on (a) weight loss of the artificial MSW and (b) Cd partitioning.

heavy metals from the waste and their incorporation into the flue gases are influenced by many factors, such as volatility, combustion conditions and ash entrainment [11–13]. Volatile cadmium compounds with high vapor pressures and low boiling points are most likely to be found in the flue gas, in contrast to metals with low vapor pressure and boiling points, such as Fe and Cu, which are almost completely trapped in the bottom ash [1–3]. The particles and the volatilized Cd produced from combustion were carried out of the burner tube by the combustion gas, and thus eliminated from the furnace immediately after their releases. The small increase in Cd volatilization with combustion time can be explained by the quick-release rate of Cd during incineration. It has been experimentally shown that metal vaporization rate is very high initially and then slows during waste incineration [12,19]. In particular, the particles shrink rapidly in the case of organic matrix burning, and the metallic compounds are released into the gas stream without any limitation [12]. After the initial combustion period (where metal release rate peaked), increasing the incineration period only had an insignificant effect on Cd volatilization. For the rest of this study, the incineration time was kept at 12.0 min, which is sufficient for near complete waste combustion.

Fig. 3a shows the distribution of Cd among the bottom ash, fly ash and flue gas as a function of incineration temperature. Temperature affects the vapor pressures and stabilities of Cd

compounds and thus the partitioning of Cd. As the temperature increased from 350 to 950 °C, the fraction of Cd in the bottom ash decreased from 53% to 11%, while that in the fly ash increased from 47% to 81%. About 8.5% of Cd was present in the flue gas at 950 °C, while no Cd was found in the flue gas at lower temperatures.

The equilibrium composition of the cadmium species as a function of incineration temperature calculated using CHEMKIN software is shown in Fig. 3b. Equilibrium composition represents the most stable chemical composition within a system under a specific set of conditions. The calculated equilibrium composition would reveal the preferred chemical speciation under a specific state, which in turn, suggests potential chemical reactions that may occur within the system [23]. The equilibrium calculation results show that $\text{CdCO}_3(\text{s})$ is the dominant species at temperatures below 250 °C and it decomposes completely at above 427 °C. $\text{CdO}(\text{s})$ becomes the only Cd species between 427 and 727 °C. Above 800 °C, $\text{CdO}(\text{s})$ begins to undergo significant decomposition and the fraction of $\text{Cd}(\text{g})$ increases with temperature. At temperatures higher than 950 °C, $\text{Cd}(\text{g})$ becomes dominant and co-exists with small fractions of $\text{CdO}(\text{g})$. These results qualitatively explain the experimental observations that Cd partitioning on fly ash increased with temperature and that Cd started to appear in the flue gas at 950 °C.

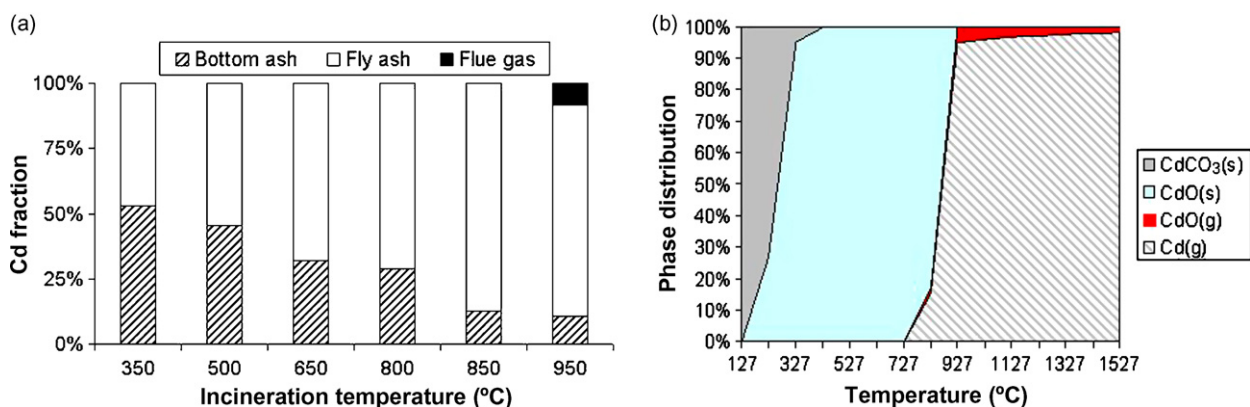


Fig. 3. Effect of temperature on Cd partitioning: (a) experimental results of Cd distribution among bottom ash, fly ash, and flue gas during incineration of the artificial MSW and (b) phase diagram for Cd speciation.

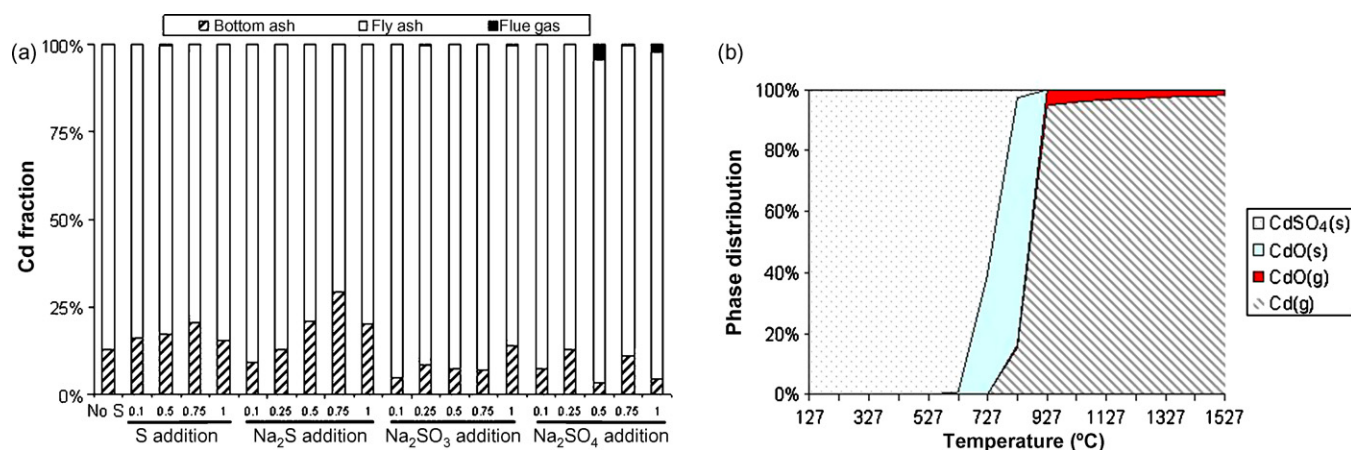


Fig. 4. Effect of sulfur on Cd partitioning: (a) experimental results of Cd distribution among bottom ash, fly ash, and flue gas in the presence of different sulfur compounds at 850 °C during incineration of the artificial MSW and (b) phase diagram for Cd speciation in the presence of sulfur.

4.2. Impact of sulfur compounds

Fig. 4a shows the partitioning of Cd among bottom ash, fly ash and flue gas in the presence of 0.1–1.0% sulfur in the forms of S, Na₂S, Na₂SO₃ and Na₂SO₄ after incineration of the synthetic wastes. Under all the conditions studied, more than 70% of Cd was associated with the fly ash. The chemical speciation of metals in the incinerator off-gas is strongly influenced by the presence of compounds of chlorine, sulfur, nitrogen, fluorine and others during combustion and gas cooling [28]. The presence of 0.5–1% S and Na₂S caused greater Cd accumulation in the bottom ash compared to the case in the absence of sulfur. In contrast, the presence of sulfur in the forms Na₂SO₃ and Na₂SO₄ apparently reduced Cd association with the bottom ash. Reaction between Cd and Na₂SO₃/Na₂SO₄ led to the formation of unstable CdSO₄. Only small fractions (<4.3%) of Cd were found in the flue gas when Na₂SO₃ and Na₂SO₄ were present. These observations suggest that the valency state of sulfur in the artificial MSW may play a role in controlling Cd volatilization during incineration. The greater accumulation of Cd on the bottom ash in the presence of S and Na₂S probably resulted from Cd fixation in the form of CdS. Although sulfides cannot play a significant role in the oxidizing conditions that prevail in the incineration furnace [29], local reducing environment can be created in the furnace if the feed is not homogeneous or the heavy metals are mixed with plastics, paper, etc. [29]. This may allow at least a portion of the sulfur to be retained within the bottom ash in its reduced or sulfide form.

Cd speciation is strongly influenced by the gas atmosphere. Fig. 4b shows the equilibrium calculation results of Cd speciation in the temperature range of 127–1527 °C in the presence of sulfur. CdSO₄(s) is the dominant Cd species at low temperatures (<650 °C), while CdO(s) starts to form from CdSO₄(s) decomposition between 627 and 927 °C. Cd(g) starts to appear at temperatures higher than 727 °C and becomes the dominant Cd species at >900 °C. These results indicate that the presence of sulfur stabilizes Cd in sulfate phase at low temperature (<650 °C), but that it has no influence at above 800 °C. Comparison of Figs. 3b and 4b suggests that the presence of S barely

affects the formation of gaseous Cd species. That is why the partitioning behavior of Cd was only slightly modified by the presence of Na₂SO₃ and Na₂SO₄. It should be noted that the influence of S and Na₂S on Cd speciation could not be shown with the thermodynamic equilibrium analysis here because of the oxidizing conditions (i.e., they would be readily oxidized).

Fig. 5 shows SEM photomicrograph of the bottom ash particles from incineration of the artificial MSW with the presence of elemental sulfur, and the results of EDS analysis. Some particles were well rounded, spherical in shape, and their surfaces appeared to be smooth; others were shaped as flowers with thin walls. For the spherical particles (A), Ca, S and O were the major elements while Cd was not detected. In contrast, the flower-shaped particles (B and C) were mainly composed of Ca, Al and S, and significant amounts of Cd as well. These results indicate elemental sulfur present in the artificial MSW was not completely oxidized to SO₂ (which would be readily carried out of the burner tube). Instead, a fraction of the sulfur formed compounds with Cd (and other metal cations as well). The facts that the only the addition of Na₂S and S increased Cd partitioning on the bottom ash while the presence of Na₂SO₃ and Na₂SO₄ reduced Cd association with the bottom ash suggest that CdS formed under locally reducing conditions during incineration of the artificial MSW when Na₂S and S were present, which delayed the volatilization of Cd. Retention of sulfur in sulfide form in the bottom ash has been observed in incineration of carbonaceous materials. For example, Kistler and co-workers observed that only ~40% CdS vaporized while pyrolyzing sewage sludge at 625 °C with local reducing environment resulted from char formation [30]. Sulfide was also found as a predominant anion species (15–20 wt.%) in the incinerator fly ash at the Idaho National Engineering and Environmental Laboratory [31].

4.3. Impact of chlorine compounds

Chlorine and hydrochloric acid can be released from combustion of plastic, especially PVC, and from cooking salt during MSW incineration. Chlorine concentrations (800–1200 mg/m³)

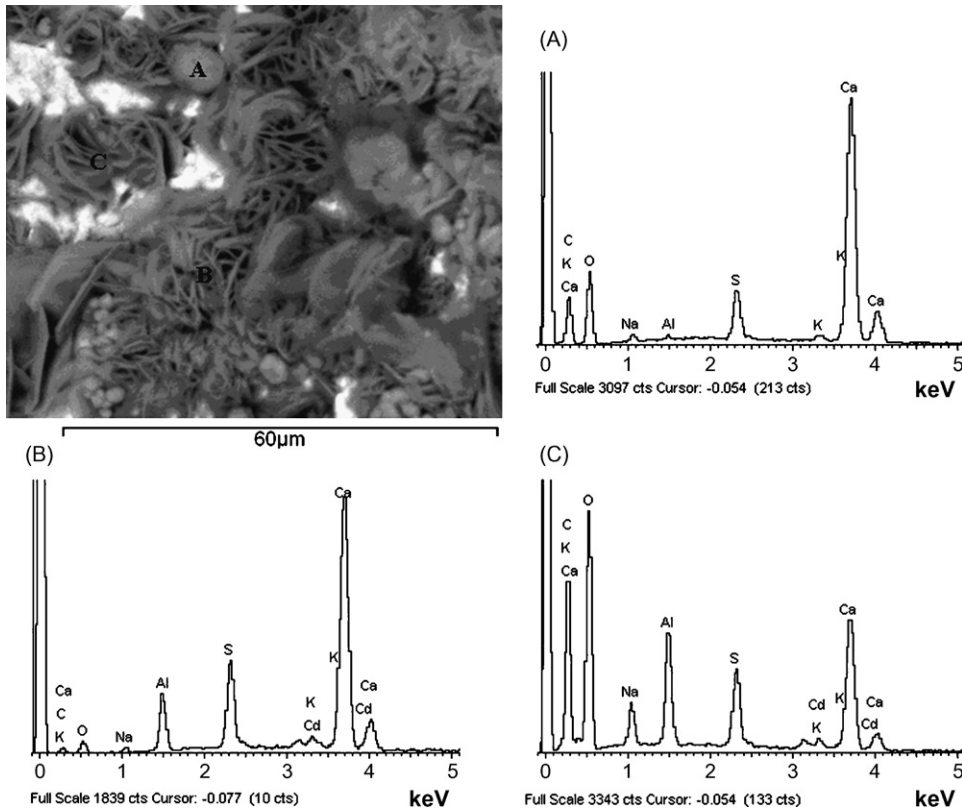


Fig. 5. Scanning electron micrograph of the bottom ash from incineration of the artificial MSW with the presence of elemental sulfur, and the results of EDS analysis for points labeled A, B, and C on the sample surface.

in typical MSW incineration chambers are high enough to allow formation of metallic chlorides [1]. Fig. 6a shows the partitioning of Cd among the bottom ash, fly ash and flue gas in the presence 2–8% chlorine in the forms of NaCl and PVC after waste incineration. In contrast to when sulfur compounds were present, about 99% of Cd was associated with the fly ash in the presence of Cl under all the conditions studied. Chlorine has a strong influence on the heavy metal partitioning because all metal chlorides generally have higher vapor pressures than their corresponding oxides [1,13].

Fig. 6b shows the equilibrium distribution of Cd in the presence of Cl. Gaseous CdCl₂ is the major species between 400 and 1000 °C; at higher temperatures, Cd(g) becomes the dominant

species with decomposition of CdCl₂ and CdO. Cd is primarily in the vapor phase at temperatures higher than 400 °C in the presence of Cl. These results indicate that Cl binds strongly with Cd and significantly increases the volatility of Cd at temperatures above 400 °C. Little Cd was found in the bottom ash at 850 °C in the presence of chlorine because Cd mainly combined with Cl in the form of volatile CdCl₂ salt with a minor fraction existing as Cd(g). Comparison of Figs. 3b and 6b suggests that Cl significantly increases the volatilization of Cd and thus its partitioning on the fly ash. Therefore, the presence of chlorine compounds worsens Cd emission during MSW incineration, consistent with the findings of previous studies [1,12,13,15,29].

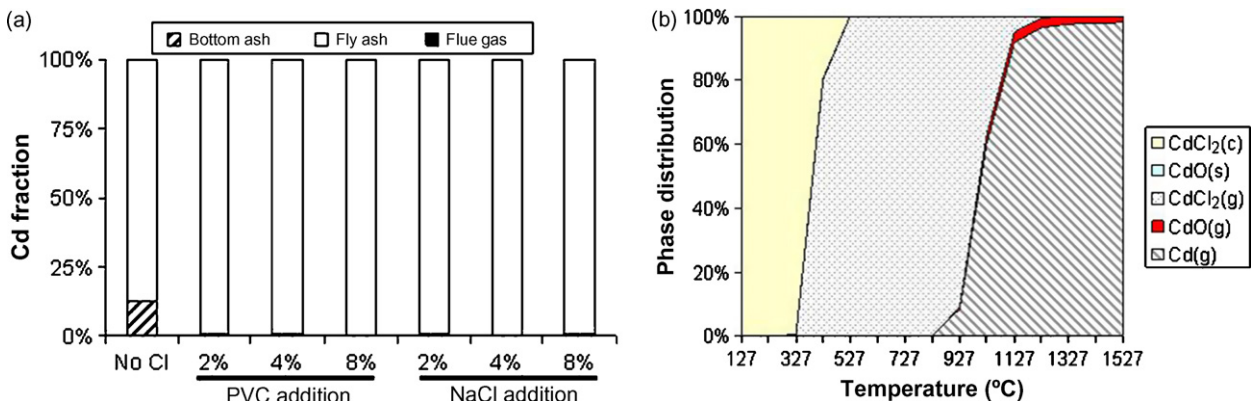


Fig. 6. Effect of chlorine on Cd partitioning: (a) experimental results of Cd distribution among bottom ash, fly ash, and flue gas in the presence of PVC and NaCl at 850 °C during incineration of the artificial MSW and (b) phase diagram for Cd speciation in the presence of chlorine.

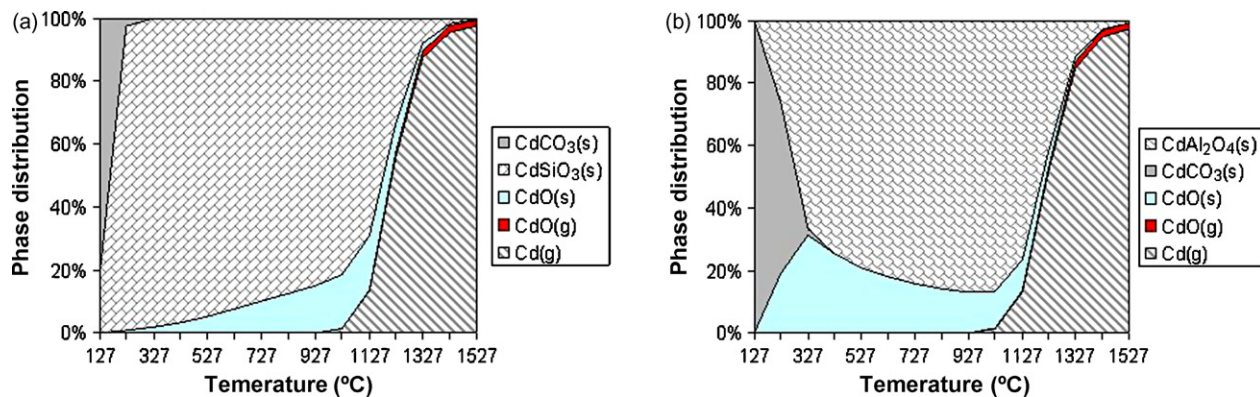


Fig. 7. Phase diagrams for Cd speciation when (a) SiO_2 and (b) Al_2O_3 are present in the artificial MSW functions as a sorbent during incineration.

4.4. Impact of sorbents (SiO_2 and Al_2O_3)

The mineral matter content of waste affects the heavy metal partitioning through formation of binary or ternary oxides that can greatly decrease the volatilization of metals [29,32]. In particular, fluidized bed incinerators provide intensive mixing, which enhances the contact between the MSW components and metal compounds during incineration. The chemical reactions occurring between the mineral matter and heavy metal species could not be studied in the laboratory tubular furnace reactor due to lack of mixing. Nonetheless, thermodynamic calculations could be carried out to simulate these processes. Fig. 7 shows that the presence of SiO_2 and Al_2O_3 can lead to the formation of stable cadmium salts ($\text{CdSiO}_3(\text{s})$ and $\text{CdAl}_2\text{O}_4(\text{s})$) in the temperature range of 300–1200 °C. That is, the chemical reactions between Cd and SiO_2 and Al_2O_3 present in the inert fraction of the MSW can significantly stabilize its volatilization. At 850 °C, approximately 85% of Cd could be bound in the form of $\text{CdSiO}_3(\text{s})$ or $\text{CdAl}_2\text{O}_4(\text{s})$ in the presence of SiO_2 and Al_2O_3 , respectively. These results indicate that the silica- and aluminum-containing materials in MSW can potentially reduce the volatilization of Cd during MSW incineration.

Fig. 8a shows the equilibrium distribution of Cd during incineration of the artificial MSW with both SiO_2 and Al_2O_3 present functioning as sorbents. $\text{CdSiO}_3(\text{s})$ is the major compound at temperatures below 900 °C, while $\text{Cd}(\text{g})$ becomes the major

Cd species at above 1200 °C. Below 1100 °C, Cd is mainly present as $\text{CdSiO}_3(\text{s})$, $\text{CdAl}_2\text{O}_4(\text{s})$ and $\text{CdO}(\text{s})$ solids. The presence of sulfur and chlorine significantly alters the distribution of Cd species and increases its volatility (Fig. 8b). In combustion environment, chlorine is known to react with heavy metals forming volatile salts that do not interact significantly with the mineral matter [1]. $\text{CdSO}_4(\text{s})$ is the dominant Cd compound at temperatures below 600 °C, while $\text{CdSiO}_3(\text{s})$, $\text{CdAl}_2\text{O}_4(\text{s})$ and $\text{CdO}(\text{s})$ coexist with $\text{CdCl}_2(\text{g})$ between 600 and 1100 °C. Above 1200 °C, $\text{Cd}(\text{g})$ becomes the dominant Cd species and its fraction increases with temperature. Less than 35% of Cd exists in the vapor phase at below 1100 °C in the presence of both sulfur and chlorine because of the reactivity of SiO_2 and Al_2O_3 . These results show that the presence of chlorine significantly increases the volatilization of Cd under MSW incineration conditions. They also indicate the importance of SiO_2 and Al_2O_3 at reducing the volatilization tendency of Cd. Therefore, the presence or addition of SiO_2 - and Al_2O_3 -containing minerals should be effective at controlling Cd volatilization during MSW incineration.

4.5. Implications of thermodynamic analysis for Cd control

The thermodynamic analysis can reasonably predict the volatilization tendency of Cd at high temperatures and qualitatively explain its general behavior in the presence of sulfur

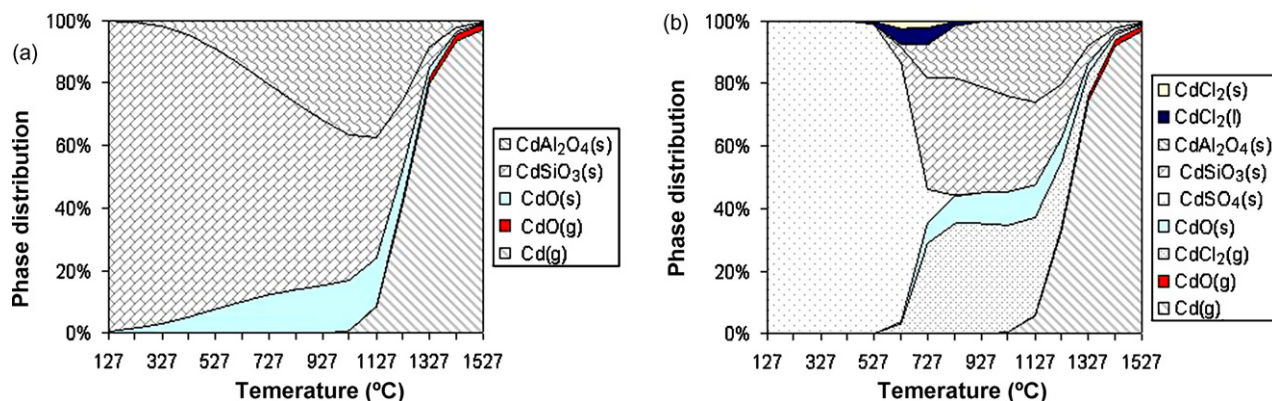


Fig. 8. Phase diagrams for Cd speciation during incineration of the artificial MSW: (a) when both SiO_2 and Al_2O_3 are present in the artificial MSW function as sorbents and (b) in the presence of sulfur and chlorine when both SiO_2 and Al_2O_3 function as sorbents.

and chlorine during MSW incineration. Thermodynamic analysis can be used as a guide to the development of pollution control strategies in MSW incineration. Simulation results indicate that the use of solid sorbents appears to be a promising technology for reducing the emissions of metal vapors in the high-temperature flue gases. CdO(s), CdAl₂O₄(s) and CdSiO₃(s) can form from chemical reactions between Cd compounds and SiO₂- and Al₂O₃-containing minerals in combustion environment. Silica sand, kaolinite, bauxite and zeolites have been observed to retain Cd effectively at high temperatures [33–37]. Obviously, the adsorption efficiency of the sorbents is influenced by factors such as operating temperature, the chlorine or sulfur content in the feed and the nature of the sorbents. A more comprehensive study on the formation of solid complex compounds and the effect of specific conditions are desirable to answer more specific questions.

From the experimental results and thermodynamic calculations, the volatilization of Cd is related to the volatility of heavy metal species formed at high temperatures and the chemical reactivity with the sorbent materials. Metal transfer during incineration is influenced by an array of processes, including volatilization, condensation, physical deposition, diffusion, adsorption (both physical and chemical) and chemical reactions in the combustion chamber [36,37]. Physical processes, such as adsorption, particle nucleation and agglomeration, which also affect the Cd partitioning, are not considered in the thermodynamic equilibrium analysis. The thermodynamic calculations also assume homogeneous conditions in a closed system and cannot account for the impact of particle sizes (which can create concentration and/or temperature gradients and non-equilibrium conditions). For example, local reducing environment allowed formation of CdS in the presence of S and Na₂S, which reduced the overall Cd volatilization during incineration, while thermodynamic equilibrium analysis could not account for this effect. Thermodynamic data of relevant species may not be available, and it is often necessary to fit for the required thermodynamic parameters from existing data. Despite these limitations, for a multi-component and multi-phase complex system such as MSW incineration, a thermodynamic approach is the only computational way to study the elemental chemistry [1]. With representative operating conditions set up in thermodynamic equilibrium models, they can reduce expenses required for conducting the emission testing of heavy metals, and determine the optimum operating conditions during incineration of wastes in the field.

5. Conclusions

Experimental investigation and thermodynamic equilibrium calculations were carried out to identify the impact of sulfur and chlorine compounds on cadmium transfer during MSW incineration. According to the experimental results, elemental sulfur and sulfide could increase the retention of Cd on bottom ash through formation of CdS under local reducing environment in the furnace. In contrast, the presence of sulfur in the forms of Na₂SO₃ and Na₂SO₄ had little effect on Cd volatilization. Chlorine compounds were observed to significantly increase Cd

volatilization and partitioning on fly ash during MSW incineration. The chemical equilibrium calculations indicate that sulfur can stabilize Cd in the form of CdSO₄(s) at low temperatures (<650 °C), while chlorine significantly increases the volatilization of Cd between 400 and 1000 °C through formation of gaseous CdCl₂. The equilibrium calculation results also suggest that SiO₂- and Al₂O₃-containing materials can function as sorbents stabilizing Cd as condensed phase solids in the temperature range of 600–1100 °C even in the presence of chlorine compounds. Comparison of equilibrium calculation results with those from experimental investigation shows that this approach gives a good qualitative view of the Cd behavior during MSW incineration. Complicated chemical and physical processes are involved within the MSW incinerator. Thermodynamic analysis is a useful tool in understanding the behavior of heavy metals during MSW incineration and can help development of better heavy metal control strategies.

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