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Stability of heavy metals in bottom ash and fly ash under various incinerating conditions

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Abstract

High chloride concentrations are normally found in municipal waste. Most chloride resources are originally derived from organic chlorides, e.g., PVC and inorganic chlorides, or chloride salt from kitchen waste. Heavy metals can easily react with chlorides during incineration, thus, producing related metallic chlorides. These factors make the combustion products more complicated (such as metallic chloride, metallic oxide, or heavy metal). This study evaluates the effects of operating conditions on the stability of heavy metals (Pb, Cd and Cr) in bottom ash and fly ash. The parameters evaluated include (1) the additives of inorganic chloride ($CaCl_2$ and NaCl) and organic chloride (PVC), and (2) various operating temperatures. The experimental results indicate that adding organic chloride (PVC) increased the leaching rates of Cr, Pb and Cd in bottom ash, but decreased this rate in fly ash. The addition of sodium chloride (NaCl) increased the leaching rates of the three metals in fly ash, but only Cr and Cd increased in bottom ash. The other inorganic chloride ($CaCl_2$) increased the leaching rate of Cr in bottom ash and fly ash, but for Pb and Cd decrease. In addition, the TCLP leaching rates of these three metals did not have an obvious relation between the total amount of original metals existed in bottom ash and fly ash and operating temperatures of incinerator, but did relate to the chemical species of the formed products. © 1998 Elsevier Science B.V.

Keywords: TCLP; Organic chloride; Inorganic chloride; Temperature; Heavy metal

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1. Introduction

Locating waste landfills in Taiwan has become extremely difficult owing to limited land space. As an alternative, incineration has the advantages of reduction in waste volume and stability in resulting ash. However, without waste separation, heavy metals can be introduced into an incinerator. The subsequent transformation and vaporization of volatile metals depend on the incineration environment. Some metals may be adsorbed by incombustible materials and left in bottom ash. Other metals may escape with flue gas, when passing through its dewpoint to form nuclei, or they may condense around existing particles, which can be removed by an air pollution control device as fly ash. As a result, bottom and fly ash could be toxic. Determining the stability of such wastes before being sent to landfills is a relevant task. If the leached concentrations of these wastes as measured by the Toxicity Characteristic Leaching Procedure (TCLP) are lower than regulatory limits, they can be directly placed in the landfill; otherwise, further processing is required. Without adequate treatment, the leachates of toxic heavy metals are potentially hazardous.

The partitioning of heavy metals in incineration systems depends on their physical and chemical properties, such as saturated vapor pressure and boiling point. Heavy metals with higher saturated vapor pressure (e.g. Hg, Cd, and Pb) are easily volatilized and enter the flue gas after combusting, which accounts for their greater content in fly ash than in bottom ash. On the other hand, metals with higher boiling points (e.g. Cr, Mg, and Cu) remain primarily in the bottom ash [1–5].

Heavy metals can react with chlorine, sulfur, and oxygen during incineration, subsequently producing various compounds. Chlorine has a significant effect on the behavior of these metals. Greenberg et al. [6] indicated that high concentrations of HCl in the gas stream may have a volatile effect on heavy metals. The HCl concentration in the combustion gases from burning is 10^2–10^3 mg/m^3, i.e. sufficiently high to form metal chlorides in the combustion chamber. Fournier et al. [7] indicated that increasing the chlorine in the feed (e.g. tetrachloro-ethylene and chloro-benzene) would increase the volatility of some volatile metals (e.g. cadmium, lead, and bismuth) and less volatile ones (e.g. copper). Besides, chlorine appeared to decrease the particle size of fly ash. Therefore, the chlorine content and form in wastes play an important role in the partitioning of heavy metals in the incineration system. Polyvinyl chloride (PVC) is one source of organic chlorine contained in municipal solid waste. A previous work has indicated that PVC can produce gaseous hydrogen chloride during combustion [8]. Inorganic chlorides, such as NaCl, in food trash or refuse, have been suggested to lead toward the formation of HCl during combustion [9]. PVC (organic chlorine) and NaCl (inorganic chlorine) are the primary sources of chlorine-containing materials.

Many methods can be used to evaluate the stability of heavy metal products after incineration, such as the EP (Extraction Procedure) [10], the TCLP (Toxicity Characteristic Leaching Procedure) [11], and the ASTM D-3987-85 [12]. These procedures employ static methods. Some studies [13] propose that the Hazard Assessment Test should accompany the static method. Many procedures [14] have been used to reduce the leached amounts of heavy metals, e.g. solidification of incineration residues and high-temperature stabilization of wastes (vitrification). It was found that various extraction fluids, buffering capacities of the ash, and some of physical characteristics of fly ash and bottom ash including specific surface area, porous size, particle sizes and amount of carbon, have great effects on the leaching rate of metals in the ash. However, not many studies addressed the effects of operating temperature and amount of chlorine on the stability of heavy metals in bottom ash and fly ash.

This study examines the stability of heavy metals (Pb, Cr, and Cd) in incineration ash. This ash was produced by incinerating waste containing heavy metals under various conditions in a fluidized bed incinerator. The TCLP was used to evaluate the stability of the heavy metal products in collected bottom ash (in sand bed) and fly ash (in cyclones).

2. Experimental

2.1. Preparation of synthetic feed wastes

The input synthetic solid wastes tested were composed of sawdust, plastics, water (to simulate ordinary municipal solid waste) and three investigated metals nitrate of 0.5 wt.% dissolved in the water. The samples were enclosed in a polyethylene (P.E.) bag of 0.3 g. Table 1 lists the composition of the various artificially composed feedstocks and operating parameters. The PVC and PP plastics used were commercially available rigid plastic raw material grains used for manufacturing. The grain size is about 0.5 cm in diameter.

2.2. Apparatus

Fig. 1 illustrates the incineration system. The fluidized bed reactor consists of a feeder, a preheated chamber (50 cm in length), a main combustion chamber (100 cm in height; 10 cm in I.D.), and a secondary combustion chamber (100 cm in height; 25 cm in I.D.). The chambers were made of stainless steel (AISI 310) walls of 3 mm in thickness. The incinerator was fitted with a perforated stainless steel gas distributor. The

Table 1
Composition of synthetic wastes and operating parameters

Run no.	Temperature(°C)	Chlorine content	Sawdust	PP	PVC	NaCl	$CaCl_2$	Water	P.E. bag
1	$T1 = 600$ $T2 = 700$	0%	1	0.7	0	0	0	1	0.3
2	$T1 = 600$ $T2 = 800$	0%	1	0.7	0	0	0	1	0.3
3	$T1 = 600$ $T2 = 900$	0%	1	0.7	0	0	0	1	0.3
4	$T1 = 700$ $T2 = 800$	0%	1	0.7	0	0	0	1	0.3
5	$T1 = 600$ $T2 = 800$	5% PVC	1	0.55	0.15	0	0	1	0.3
6	$T1 = 600$ $T2 = 800$	10% PVC	1	0.4	0.3	0	0	1	0.3
7	$T1 = 600$ $T2 = 800$	5% NaCl	1	0.55	0	0.15	0	1	0.3
8	$T1 = 600$ $T2 = 800$	10% NaCl	1	0.4	0	0.3	0	1	0.3
9	$T1 = 600$ $T2 = 800$	5% $CaCl_2$	1	0.55	0	0	0.15	1	0.3
10	$T1 = 600$ $T2 = 800$	10% $CaCl_2$	1	0.4	0	0	0.3	1	0.3

$T1$ = Sand bed temperature; $T2$ = Freeboard temperature; unit: g. ($T1$ and $T2$ have a range ±20°C.)

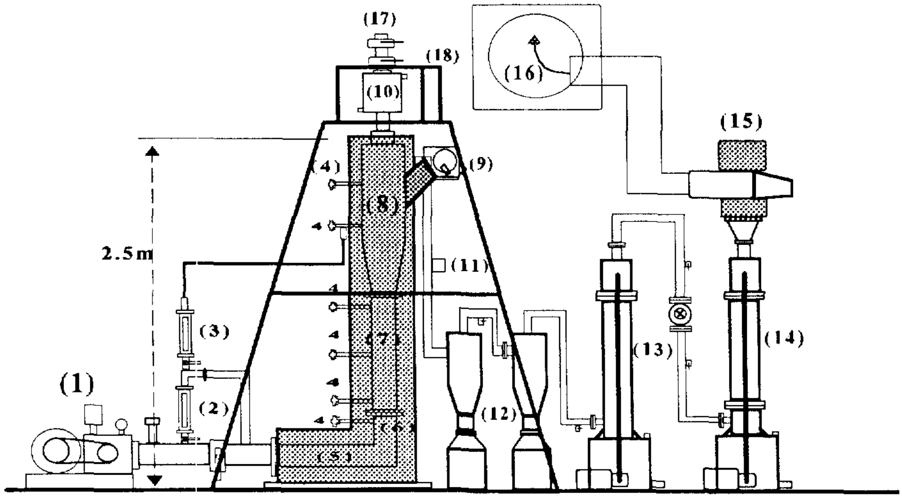

Fig. 1. The fluidized bed incinerator. Explanation: (1) blower, (2) flow meter for first air, (3) flow meter for 2nd air, (4) thermal x couples, (5) air preheated chamber, (6) air distributor, (7) first combustion chamber (sand bed zone), (8) 2nd combustion chamber (freeboard), (9) gas burner, (10) cooling system for feeding, (11) flue gas sampling site, (12) cyclones, (13) cooling tower, (14) scrubber, (15) I.D. fan, (16) exhaust site, (17) feeding site, (18) feeding stage.

static bed height was 70 cm, and the expanded bed height was about 90 cm. Six thermocouples were used to determine the temperature profiles in the preheated chamber, sand bed, and freeboard. The combustion gas was treated by two consecutive cyclones and a wet scrubber, and then released into atmosphere.

2.3. Experimental procedure

The excess air value of 25–40% was determined by calculating the theoretical air required. This is around 40 l/min of air input at room temperature. Comparing the temperature effects reveals that the main combustion chamber is controlled at 600°C and 700°C(±20°C), and the freeboard zone from 700°C to 900°C (±20°C). Synthetic waste was fed in at 20-s intervals. When investigating the effects of chlorine-containing materials, the main combustion chamber was controlled at 600°C (±20°C), and the freeboard zone at 800°C (±20°C).

First, when the main combustion chamber was heated to the desired temperature by the electrical heaters, the gas burner was turned on to raise the freeboard temperature. Next, the synthetic waste without metals was fed to the incinerator. After the temperature reaching the steady state, the fly ash in the cyclones was cleared out; the wet scrubber pump was turned on, and the metal-containing synthetic wastes were added. The experiment was continuously performed for 50 min. Following the experiment, the bottom ash (in sand bed) and fly ash (in cyclones) were accumulated to measure the concentration of three metals by atomic absorption spectroscopy (A.A.S.) and their leaching rates by TCLP.

The total amount of inorganic metals in the sample were measured by the following method. First, the bottom ash and fly ash were completely mixed individually, three representative samples were taken out, then digested by microwave digestion (USEPA Method 3051) [15], after that, the metals' concentration were measured by A.A.S.. The final metals' concentration were determined by averaging values of three measurements.

2.4. TCLP Leaching Test

To understand the stability of heavy metals produced by incineration more thoroughly, the TCLP was used [11]. The obtained leachates were pretreated by microwave digestion [15]; their heavy metal concentrations were then measured. The leaching rate is defined as the amount of metal in the leachate/the total amount of metal in the sample. The stability of heavy metal products in bottom and fly ash can be judged according to the leaching rate. The obtained leachates were further measured to identify their chloride salts by mercury nitrate titration.

3. Results and discussion

Table 2 lists the Pb, Cd, and Cr distributions in bottom ash and fly ash under various incinerating conditions. Also, Figs. 2–5 displays the Pb, Cd, and Cr leaching rates of TCLP under various incinerating conditions. These results are discussed below.

3.1. Comparison between the distributions of heavy metal and leaching rates of TCLP in bottom ash and fly ash under various operating temperatures

3.1.1. In bottom ash

Table 2 indicates that operating temperatures do not have a significant effect on the metal distribution in bottom ash. However, the distributions of different metal species

Table 2
Metal distribution in silica sand and fly ash under various operating conditions

Run no.	Operating condition	Pb		Cr		Cd	
		Silica sand	Fly ash	Silica sand	Fly ash	Silica sand	Fly ash
1	$T1 = 600$ $T2 = 700$	82.01%	9.20%	62.11%	9.29%	35.98%	8.65%
2	$T1 = 600$ $T2 = 800$	81.69%	9.88%	60.32%	9.85%	35.62%	8.71%
3	$T1 = 600$ $T2 = 900$	81.68%	9.68%	59.11%	9.56%	34.19%	8.91%
4	$T1 = 700$ $T2 = 800$	83.21%	9.21%	64.50%	11.03%	28.65%	10.69%
5	PVC 5%	70.21%	10.95%	46.12%	10.69%	24.36%	14.21%
6	PVC 10%	70.66%	11.35%	49.68%	11.68%	23.11%	13.89%
7	NaCl 5%	79.86%	6.31%	69.78%	6.88%	45.21%	7.54%
8	NaCl 10%	80.21%	7.62%	72.19%	5.69%	52.09%	7.21%
9	CaCl2 5%	78.31%	6.51%	78.60%	5.61%	59.86%	7.13%
10	CaCl2 10%	75.12%	6.98%	77.30%	6.13%	57.77%	6.55%

Run 5–Run 10 were controlled at $T1 = 600$, $T2 = 800$.

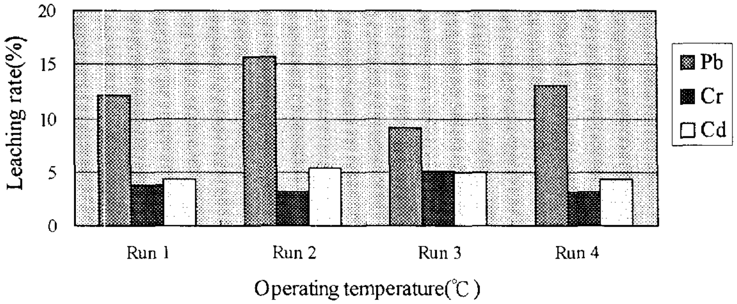

Fig. 2. The effect of operating on TCLP leaching rate for Pb, Cd and Cr in bottom ash.

(Pb, Cd, and Cr) are quite different. In bottom ash, the distributions of Pb, Cd, and Cr are in the neighbourhood of 80%, 60%, and 30%, respectively. Fig. 2 summarizes the effects of operating temperature on TCLP leaching rate for Pb, Cd and Cr in bottom ash. For Pb, when $T1 = 600°C$ and $T2 = 900°C$, it has the lowest leaching rate among all operating temperatures. For Cd and Cr, various incinerating temperatures have no significant effect on the leaching rate. Comparing these three metals in this temperature range, Cd and Cr are more stable than Pb because they have smaller leaching rates.

3.1.2. *In fly ash*

Table 2 reveals that all three heavy metals have almost the same distribution ratio under various operating temperatures. However, Fig. 3 shows the leaching rates of these three metal species under various operating temperatures are quite different. For fly ash, the leaching rate of Cd is the highest, then Pb, followed by Cr. This would suggest that Cr is the most stable one in fly ash, Pb the second, and Cd the least. This phenomenon is quite different from bottom ash. In bottom ash, Cr and Cd were more stable than Pb. Perhaps this is due to that metal species formed in bottom ash and fly ash are different. The trend of the leaching rate under various incinerating temperatures was quite random.

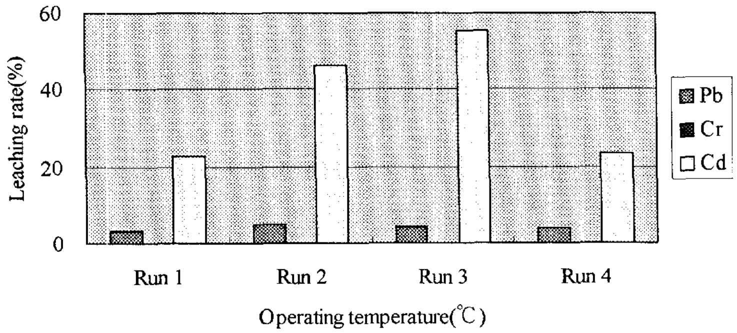

Fig. 3. The effect of operating temperature on TCLP leaching rate for Pb, Cd and Cr in fly ash.

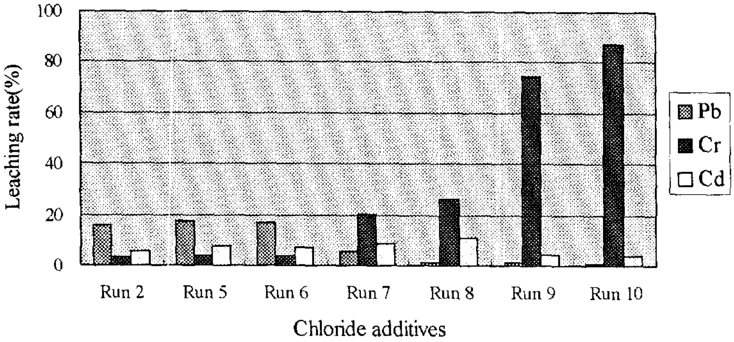

Fig. 4. The effect of PVC, NaCl and $CaCl_2$ on TCLP leaching rate for Pb, Cd and Cr in bottom ash ($T1 = 600°C$, $T2 = 800°C$).

However, the effect of various metal species on the leaching rate is more significant than that of operating temperatures.

3.2. The influence of adding an organic chloride and inorganic chlorides (NaCl and $NaCl_2$) on metal partition and their leaching rates

3.2.1. In bottom ash

Table 2 reveals that the partition of three metal species (Cr, Pb, Cd) in bottom ash decreases by adding an organic chloride (PVC); however, adding inorganic chlorides (NaCl and $CaCl_2$) increases the partition of Cr and Cd in bottom ash, but not that of Pb. It shows that inorganic chlorides have almost no influence on Pb. Fig. 4 shows the effect of adding an organic chloride (PVC) and inorganic chlorides (NaCl and $CaCl_2$) on the leaching rates of Pb, Cd, and Cr in bottom ash. Those results demonstrate that adding an organic chloride (PVC) increases the leaching rate for all three metal species. It was

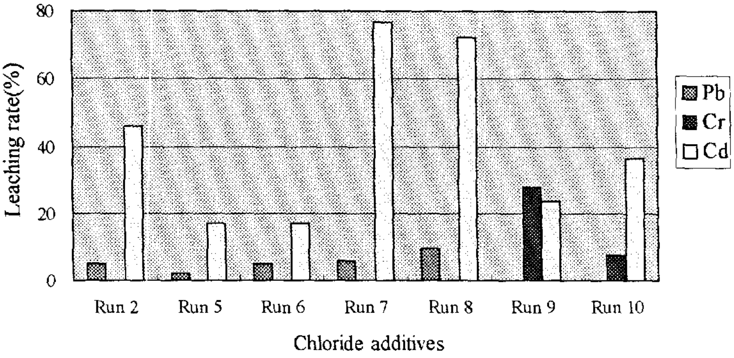

Fig. 5. The effect of PVC, NaCl and $CaCl_2$ on TCLP leaching rate for Pb, Cd and Cr fly ash ($T1 = 600°C$, $T2 = 800$ °C).

presumed that adding an organic chloride (PVC) would react with metal species to produce more easily-leachable compounds. However, adding inorganic chlorides (NaCl and $CaCl_2$) did not show a regular trend. The adding of $CaCl_2$ decreases the leaching rate of Pb obviously, but increases the leaching rate of Cr significantly. This phenomenon may be due to the various metallic species formed during incineration, or the influence of the alkaline metal Na and the alkaline earth metal Ca.

3.2.2. In fly ash

Table 2 reveals that adding an organic chloride increases the distribution amount of Pb, Cr, and Cd in fly ash during incineration; however, inorganic chlorides yield an opposite result. Fig. 5 indicates that adding an organic chloride decreases the leaching rate of all three metal species. This result is opposite to the result for bottom ash. This may be due to the compounds formed in bottom ash and fly ash are different. However, for adding inorganic chlorides, the leaching rate of the three metal species shows an irregular trend in bottom ash and fly ash. Especially, the results of adding $CaCl_2$ show that the leaching rate of Pb decreases obviously, but for Cr increases significantly. The same phenomenon in bottom ash was described above.

3.3. Chloride salt in TCLP leachates

Fig. 6 summarizes the effects of adding PVC, NaCl and $CaCl_2$ on the concentration of chloride salt in a TCLP leachate. This figure also reveals that the amount of chlorine salt from a TCLP leachate is much greater in fly ash than in bottom ash. This finding verifies that chloride products distributed in fly ash are greater than those in bottom ash. The result also indicates that adding more chloride salt would cause a higher amount of chloride ions (Cl^-) in a TCLP leachate. Besides, an addition of NaCl would increase the amount of chloride salt in a TCLP leachate of fly ash, but adding PVC would decrease the amount of chloride salt in a TCLP leachate of fly ash. Comparing Fig. 4 and Fig. 5 with Fig. 6, in bottom ash, the leaching rate of any heavy metal is not related to the amount of chloride salt in the TCLP leachate. However, in fly ash, the leaching rate of

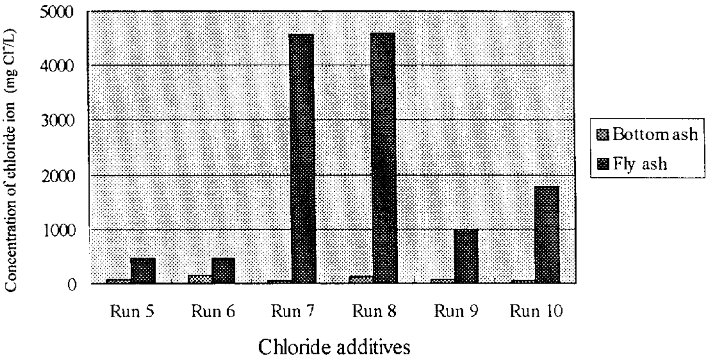

Fig. 6. The effect of PVC, NaCl and $CaCl_2$ on the chloride ion concentration (Cl^-) in TCLP leachates.

Cd is proportional to the amount of chloride salt in the TCLP leachate. When adding NaCl (5% and 10%), the leaching rate of Cd is the highest, the same as the highest amount of chloride salt content. But Pb and Cr did not show this trend. We can therefore infer that the metal products in fly ash would have a high ratio of chlorides of cadmium, and would also contain a high ratio of chloride salt.

4. Conclusions

(1) No significant correlation was found between the operating temperature and leaching rate (TCLP). However, within the range of operating temperatures tested, in bottom ash, Pb had a higher leaching rate than the other metals. Cd and Cr had almost the same rate. In fly ash, Cd has the highest leaching rate, then Pb, and Cr the lowest. That is, in bottom ash, Cd and Cr are more stable species, not easily leaching; but in fly ash, Cd is the most stable one.

(2) Adding an organic chloride would increase the leaching rates of all three metal species (Pb, Cr and Cr) in bottom ash, but decrease the rates in fly ash. However, adding inorganic chlorides (NaCl and $CaCl_2$) showed an irregular trend of leaching rates both in bottom ash and fly ash. This irregular trend was due to various metallic species with different leaching characteristics and different kinds of inorganic chlorides added (NaCl and $CaCl_2$). Moreover, an addition of $CaCl_2$ causes extraordinary leaching rates of Pb and Cr.

(3) The leaching rate of Cd in fly ash is proportional to the amount of chloride salt in the TCLP leachate.

(4) The leaching rate of TCLP in these metals did not exhibit an obvious relation to the total amount of the original metal, but did relate to the chemical species of the product. More sophisticated analytical methods need to be used to distinguish between different species of the same metal.

References

[1] H. Vogg, H. Braun, M. Metzger, J. Schneider, The specific role of cadmium and mercury in municipal solid waste incineration, Waste Manage. Res. 4 (1986) 65.

[2] R. Barton, W.D. Clark, W.R. Seeker, Fate of metals in waste combustion systems, Combust. Sci. Tech. 14 (1990) 327.

[3] S.L. Law, G.E. Gordon, Sources of metals in municipal incinerator emissions, Environ. Sci. Technol. 13 (1976) 432.

[4] M.A. Vancil, C.R. Parrish, M.A. Palazzolo, Emissions of Metals and Organics from Municipal Wastewater Sludge Incinerator, July, 1991, US EPA/600/S2-91/007.

[5] W.P. Linak, O.L. Jost, Toxic metal emissions from incineration: mechanisms and control, Prog. Energy Combust. Sci. 19 (1993) 145.

[6] R.R. Greenberg, W.H. Zoller, G.E. Gordon, Composition and size distributions of particles released in refuse incineration, Environ. Sci. Technol. 12 (1978) 566.

[7] D.J. Fournier, W.E. Whitworth, J.W. Lee, L.R. Waterland, The Fate of Trace Metals in a Rotary Kiln Incinerator with a Venturi/Packed Column Scrubber, Feb., 1991, US EPA/600/S2-90/043.

[8] A. Crosato-Arnaldi, G. Palma, E. Peggion, G. Talamini, Investigations on the dehydrochlorination of poly(vinyl chloride), J. Polymer Sci. 8 (1964) 747.
[9] M.Y. Wey, T.J. Fang, The effect of organic and inorganic chlorides on the formation of HCl with various hydrogen containing sources in a fluidized bed incinerator, Environ. Int. 21 (1995) 423.
[10] US EPA Federal Register, EPA-Hazardous Waste and Consolidated Permit Regulations, US EPA, Washington, DC, Monday, May 19, 1980, p. 33075.
[11] US EPA Federal Register, Rules and Regulations, US EPA, Washington, DC, Friday, 51 (1986) p. 40643.
[12] ASTM D-3987-85, Standard Test Method for Shake Extraction of Solid Waste with Water, 1985, pp. 24–27.
[13] L. Douglas, Hazardous and Industrial Solid Waste Testing and Disposal, Sixth Volume, 1986, ASTM (PCN).
[14] R.B. Pojasek, Toxic and Hazardous Waste Disposal, Vol. 2, Options for Stabilization/Solidification, Ann Arbor Sci., 1979.
[15] US EPA, Test Methods for Evaluating Solid Waste, Method 3051, US EPA, Washington, DC, November, 1986.