

Evolution and distribution characteristics of fluorine during the incineration of fluorine-containing waste in a hazardous waste incinerator*

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Abstract: In this study, the evolution and distribution of fluorine during the incineration of fluorine-containing waste in a hazardous waste incinerator were investigated. The evolution characteristics of fluorine during the pyrolysis of the waste were investigated using thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR) analysis. The distribution of fluorine in the incineration systems and its form in the incineration residues were studied under two operating conditions. The results showed that fluorine in the waste had strong volatility and hydrogen fluoride (HF) and silicon fluoride (SiF₄) were detected as the first fluorine compounds to be released during pyrolysis. The release of HF could be divided into three temperature ranges: 123.5–757.5 °C, 757.5–959.6 °C, and >959.6 °C. The emission of HF between 123.5 °C and 757.5 °C involved loosely bonded organic fluorine and ionic inorganic fluorine, while the HF released between 757.5 °C and 959.6 °C was caused by the crack of fixed carbon and further dehydroxylation, and the HF released above 959.6 °C was due to the decomposition of inorganic minerals. The emission of SiF₄ was mainly concentrated between 132.6 °C and 684.0 °C, and almost no SiF₄ was emitted from the waste above 684.0 °C. Less than 20.73% of the fluorine was retained in the incineration residues and over 79.17% of fluorine was absorbed in the absorbent solution of a wet flue gas desulfurization (WFGD) system. The amount of fluorine discharged into the atmosphere was below 0.12%. The fluorine in the bottom slag and burn-out chamber ash mainly existed in residual form. The proportions of water-soluble, exchangeable, and acid-soluble fluorine in the boiler ash and bag filter ash were both over 80%.

Key words: Fluorine emission; Hazardous waste incineration; Fluorine-containing waste; Release behavior; Distribution
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1 Introduction

With the rapid development of the fluorine chemical industry, large amounts of fluorine-containing wastes have been produced. Large quantities of harmful gaseous fluoride such as HF are exhausted into the atmosphere during the incineration of these wastes (Feng et al., 2012). The toxicity of HF to

humans and plants is 10–100 times that of sulfur dioxide (SO₂) (Guo et al., 2006). Long-term exposure to more than 0.2 μg/m³ of HF will cause damage to plants (WHO, 1996). A high incidence of endemic fluorosis related to atmospheric fluoride contaminant from combustion of high fluorine-containing coals and manufacturing of bricks and tiles has been reported in China (Finkelman, 2004; Guo et al., 2006). By sampling and analyzing undisposed waste from a hazardous waste incineration plant in Zhejiang, China, the fluorine content in the waste was found to be more than 1% in weight, which is much higher than that in coal with a mean of 150 μg/g in world coals (Swaine, 1990) and 82 μg/g in Chinese coals (Luo,

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2005). If the waste with high fluorine content cannot be properly treated, the gaseous fluoride emitted during incineration will cause serious threats to the health of nearby residents (Feng et al., 2016). In addition to environmental concerns, the released HF also gives rise to problems of equipment corrosion (Guo et al., 2006).

The hazardous waste incineration system generally features a rotary kiln coupled with a secondary combustion chamber (Feng et al., 2012). In the rotary kiln, the waste is heated to 700–800 °C for pyrolysis gasification. A reducing atmosphere is adopted in the rotary kiln to prevent slagging. Then the flue gas generated in the rotary kiln is sent to the secondary combustion chamber, where the temperature is above 1100 °C, for the complete combustion of persistent organic pollutants (Feng et al., 2016; Wang et al., 2018). Compared to the heat treatment of coals and clay materials, different fluorine contents and treatment processes can lead to different release behavior of fluorine during the incineration of fluorine-containing waste and thus it is imperative to investigate that release behavior for evaluation and control of fluorine pollution.

Fluorine in the waste is released into the flue gas and is partially enriched in the incineration residues during incineration. Previous studies (Piekos and Paslawska, 1998; Prasad, 2007) suggested that fluorine in coal fly ash was prone to leaching under landfill conditions. The leaching characteristics of fluorine are closely related to the concentration and occurrence of its different forms (Wenzel and Blum, 1992; Piekos and Paslawska, 1998; Wang et al., 2002). It is thus essential for the environmental risk assessment of fluorine emission to investigate the distribution of fluorine in the incineration systems and the forms in which it occurs in the incineration residues.

Previous research has focused on fluorine emission during the thermal treatment of coal (Bauer and Andren, 1985; Qi et al., 2002, 2003; Li et al., 2005; Guo et al., 2006) and in ceramic manufacturing (García-Ten et al., 2006; González et al., 2006; Monfort et al., 2008). Qi et al. (2002) suggested that fluorine in coal might exist in the lattice of minerals, in the form of water-soluble salts or in the form of inorganic minerals, or be absorbed on the surface of particles. Guo et al. (2006) studied the release behavior of fluorine during thermal treatments of coals in nitrogen (N₂), water vapor (H₂O), and carbon dioxide (CO₂)

atmospheres, and concluded that the release of fluorine was significantly promoted in an H₂O atmosphere. Li et al. (2005) observed that a CO₂ atmosphere was more favorable to the release of fluorine compared with an N₂ one. During the heat treatment of clay materials, Monfort et al. (2008) found that fluorine gases, in which the most abundant compound was HF, started to volatilize at temperatures 600–800 °C. García-Ten et al. (2006) suggested that adding calcium compounds favored the retention of fluorine in fluorite (CaF₂) and cuspidine (Ca₄Si₂O₇F₂) at low temperatures (850–1000 °C) during the firing of ceramic materials, whereas it was ineffective at higher temperatures as CaF₂ and Ca₄Si₂O₇F₂ are unstable above 1100 °C. Relatively little research on the evolution and distribution of fluorine during the incineration of fluorine-containing waste has been conducted.

In this study, we investigated (1) the release behavior of fluorine during the incineration of fluorine-containing waste, (2) the distribution of fluorine in the incineration systems, and (3) the occurrence form of fluorine in the incineration residues. Thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR) analysis was used to investigate the release behavior of emitted gaseous fluoride, as it monitors continuously both the time dependent evolution of the gases and the weight of non-volatile materials (Zhu et al., 2008). It has been widely used in the analysis of pyrolysis and combustion characteristics of solid fuels (Zhu et al., 2008; Tao et al., 2010; Ahamad and Alshehri, 2012). The concentration and mass distribution of fluorine in the incineration systems were investigated in a full-scale incinerator. The sequential chemical extraction (SCE) test was performed to analyze the occurrence form of fluorine in the incineration residues. The information gained from this study on the fate and mass flow of fluorine during the incineration of fluorine-containing waste can establish a foundation for further strategies for controlling fluorine pollution.

2 Experimental

2.1 Sample collection

The samples were obtained from a hazardous waste incineration plant located in Zhejiang, China. The hazardous waste was from the factories producing fluorinated chemicals near the incineration plant.

Information on the hazardous waste incineration plant is shown in Table 1. The diagram of the incineration plant is shown in Fig. 1 and the sampling points are the same as that in our previous work (Li et al., 2018).

Sampling campaigns were carried out under two operating conditions (#1 and #2). The incinerator operating temperatures during the sampling period are shown in Table 2. The waste, bottom slag, burn-out chamber ash, boiler ash, bag filter ash, and the adsorbent solution of the wet flue gas desulfurization (WFGD) system were collected at 2-h intervals. The sampling of fluorine in the flue gas was carried out according to Chinese national standard (MEE, 2013) and the sampling apparatus is presented in Fig. 2. Particulate fluorine in the flue gas was collected on the filter cartridge and 0.1 mol/L potassium hydroxide (KOH) solution was used as the absorption solution for the vapor-phase fluorine. The temperature of the sampling tube and the filter was controlled at about 185 °C to avoid the condensation of water vapor in which fluorine gas could dissolve. The pumping flow of the extraction pump was set at 1.5 L/min and the sampling time for each sample was 45 min. In addition, during the sampling of fluorine in the downstream flue of the WFGD system, a condensate collector was added in

front of the absorption bottle to collect the fluorine in the water vapor or in the droplets. The condensate was rapidly separated from the gas path to avoid the absorption of fluorine into the condensate.

2.2 Sample analysis

All the solid samples were dried in a desiccator to a constant weight at 55 °C before analysis. The bag filter ash was separated into six fractions (<75 μm, 75–106 μm, 106–150 μm, 150–270 μm, 270–550 μm, and >550 μm) by vibrating screens. The industrial and elemental analyses of the waste are shown in Table 3. High fluorine content (1.65% for #1 and 1.36% for #2) was found in the waste.

TG-FTIR analysis was conducted in a Netzsch STA 499 F3 Jupiter® (Netzsch, Germany) coupled with a Bruker Tensor (Bruker, Germany). To reduce secondary reactions, the stainless transfer pipe and gas cell (20-cm optical path length) were heated at 200 °C. Resolution of the spectrum was set as 4 cm⁻¹ within a spectral region 4000–600 cm⁻¹ and the scan frequency was set at 20 times per minute. Approximately 12 mg of the waste was used in each TG-FTIR analysis. Nitrogen was used as the carrier gas at a flow rate of 30 mL/min. A heating rate of 20 °C/min

Table 1 Information of the hazardous waste incineration plant

Disposal capability (t/d)	Furnace type	Secondary furnace outlet temperature (°C)	Flue gas cleaning system
100	Rotary kiln, secondary furnace, burn-out chamber	1100–1200	SNCR, QT, AC, BF, WFGD

SNCR: selective noncatalytic reduction; QT: quench tower; AC: activated carbon; BF: bag filter

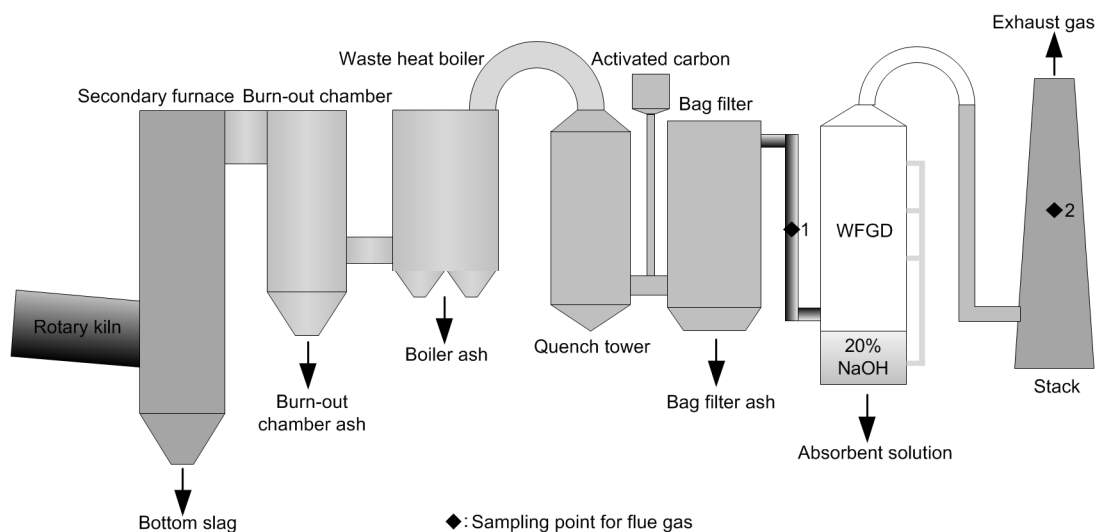


Fig. 1 Diagram of the incineration plant and sampling points

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was adopted and 1400 °C was set as the final temperature. A crucible made of α -alumina oxide was used to avoid reaction with corrosive gases at high temperature. As buoyancy is the main source of error during TG experiments (Li and Suzuki, 2009), a blank run was carried out to correct the buoyancy effect prior to the experiments with the real sample.

Table 2 Incinerator operating temperatures of #1 and #2

Condition	Temperature (°C)		
	Rotary kiln outlet	Secondary furnace outlet	Quench tower outlet
#1	771±31	1176±65	169±12
#2	769±35	1165±61	173±13

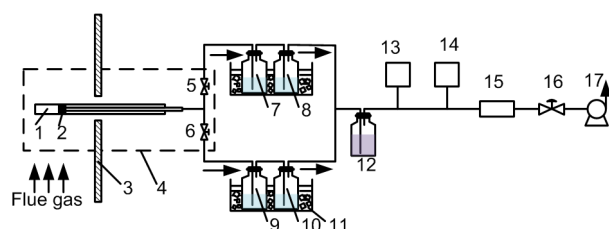


Fig. 2 Sampling apparatus for fluorine in the flue gas

1: sampling tube; 2: filter; 3: flue wall; 4: heating zone; 5 and 6: cut-off valves; 7–10: absorption bottles; 11: ice-water bath; 12: desiccator; 13: pressure sensor; 14: temperature sensor; 15: flow sensor; 16: flow control device; 17: extraction pump

Table 3 Industrial and elemental analyses of the hazardous waste (in weight, dry air basis)

Item	Value	
	#1	#2
Moisture (%)	5.35	6.89
Ash (%)	21.44	19.04
Volatile matter (%)	48.57	46.31
Fix carbon (%)	24.64	27.76
Low heating value (MJ/kg)	15.635	14.017
C (%)	28.56	27.97
H (%)	2.57	3.26
N (%)	3.42	4.66
S (%)	2.85	2.76
O (%)	35.81	35.42
F (%)	1.65	1.36
Cl (%)	2.85	3.61
Si (%)	0.64	0.81
Ca (%)	1.76	1.45
Al (%)	2.35	1.43
Na (%)	7.25	8.63

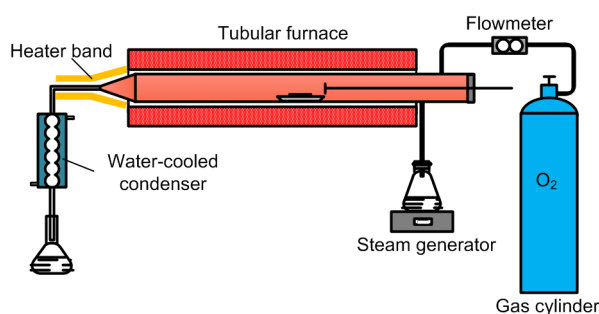
The fluorine content in the waste and incineration residues was obtained using a combustion-hydrolysis/ion chromatography (IC) method in accordance with Chinese national standard (AQSIQ and SA, 2014). The combustion-hydrolysis apparatus is illustrated in Fig. 3. An alundum tube and boats made of α -alumina oxide were used to avoid the reaction with HF at high temperature. In each test, 0.5 g sample was mixed evenly with 0.5 g quartz sand in the porcelain boat, then another 0.5 g quartz sand was laid on the surface. The porcelain boat was gradually placed in the tube furnace that had been preheated up to 1100 °C. The oxygen flow was adjusted to 400 mL/min. The evaporation of the steam generator was adjusted to control the volume of condensate at 2.5–3.0 mL/min and the volume of condensate was finally controlled within 85 mL. The pH value of the condensate was adjusted to 6 with sodium citrate and potassium nitrate solution ($C_3H_4OH(COONa)_3-KNO_3$) as a total ionic strength adjustment buffer. The fluorine concentration of the condensate was analyzed by high pressure IC (Thermo Fisher Scientific Dionex Integriion, Waltham, USA). The content of particulate fluorine on the filter was also determined by the combustion-hydrolysis/IC method. All the samples were tested three or more times to maintain the relative standard deviation within $\pm 5\%$.

A modified sequential extraction method was employed (He et al., 1998) to analyze the occurrence form of fluorine in the incineration residues. Water-soluble fluorine is composed of fluorine in the form of its ion and in complexes on the surface of particles. Exchangeable fluorine refers to the fluorine adsorbed on particles with exchangeable positive charge by electrostatic attraction, and it can be leached out in 1 mol/L $MgCl_2$ (He et al., 1998). Acid-soluble fluorine consists of the fluorine which is adsorbed on Al-, Mn-, and Fe-oxides/oxyhydroxides or retained in CaF_2 . Organically bound fluorine is composed of fluorine related to organic materials. The residual form of fluorine is likely to occur in the lattice of minerals.

A SCE test was performed on 10 g of the incineration residue using the extraction sequence shown in Table 4. In each step, 50 mL of the specific reagent was used to extract the sample and a high-speed freeze centrifuge (TGL18M, Kaida China) was used to separate the leachate from the solid. The pH

Table 4 Sequential chemical extraction scheme for the incineration residues

Step	Speciation	Reagent	Condition
1	Water-soluble	Deionized water	70 °C, rotating oscillation, 3 h
2	Exchangeable	1 mol/L MgCl ₂	25 °C, rotating oscillation, 6 h
3	Acid-soluble	0.04 mol/L NH ₂ OH·HCl in 20% HNO ₃ (in volume)	60 °C, rotating oscillation, 6 h
4	Organically bound	Pretreat the sample with 0.02 mol/L HNO ₃ and 30% H ₂ O ₂ (in volume); 3.2 mol/L CH ₃ COONH ₄	25 °C, rotating oscillation, 3 h
5	Residual		105 °C, drying in the oven, 2 h

**Fig. 3 Combustion-hydrolysis apparatus**

value of the extract solution was adjusted with C₃H₄OH(COONa)₃-KNO₃ and high pressure IC was used to determine the fluorine content in the extract solution. The fluorine content in the residual fraction was determined by the combustion-hydrolysis/IC method.

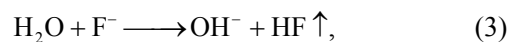
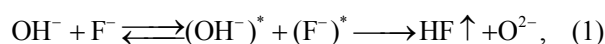
3 Results and discussion

3.1 TG-FTIR analysis

The TG and differential thermogravimetry (DTG) curves of the hazardous waste of #1 and #2 during pyrolysis are displayed in Fig. 4. The following account is illustrated by the waste sample of #1 as a similar pyrolysis process was found for both #1 and #2. The pyrolysis process of the waste was divided into three stages based on the DTG curve. The first stage was from 120 °C to 620 °C and 28.7% of weight loss occurred in this stage. It was observed from the infrared radiation (IR) spectrum at 457 °C in Fig. 5 that CO₂, SO₂, ketone, ester, ether, acid, and aldehyde were emitted in this stage, which indicated that the first stage was the fast thermal decomposition of the organic component. Meanwhile, four characteristics branches (3801.5 cm⁻¹, 3853.6 cm⁻¹, 3901.8 cm⁻¹, and 3948.1 cm⁻¹) ascribed to HF and the vibrational absorption bands of SiF₄ around 1016.4 cm⁻¹ were also

found in this stage. The second stage was from 620 °C to 820 °C and 7.6% of weight loss occurred. The characteristic bands of the functional group C=O and C-O were observed in the IR spectrum at 808 °C in Fig. 5. CO₂ and carbon monoxide (CO) were the main pyrolysis gaseous products in this stage, which indicated that the second stage was the further cracking of fixed carbon. The last stage, which was from 820 °C to the end of the heating process, was the further decomposition of the residues and inorganic minerals. The total weight loss of the sample during pyrolysis was 75.5%. During the whole pyrolysis process, the characteristic bands of fluorinated hydrocarbons, such as CF₃H and CFH₃, were not detected in the IR spectrum.

The absorbance with temperature at the characteristic wavenumbers of HF and SiF₄ was plotted as shown in Fig. 6 to investigate the evolution of HF and SiF₄ during pyrolysis. The wavenumbers corresponding to the highest absorbance for HF (3853.6 cm⁻¹) and SiF₄ (1016.4 cm⁻¹) in the IR spectrum were chosen as the characteristic wavenumbers. It was observed that the emission of HF could be divided into three stages. In the first stage, the release of HF started at 123.5 °C and increased with temperature to reach its peak value at 472.6 °C. Then it decreased gradually as the temperature rose to 757.5 °C. Qi et al. (2003) suggested that fluorine in water-soluble salts was released with the evaporation of adsorptive water and constructive water under 700 °C. The hydrolysis process of F⁻ can be described by the following chemical reactions (Qi et al., 2002):



where (OH⁻)^{*}, (F⁻)^{*}, and (H⁺)^{*} are the activated states of the corresponding ions. In addition, fluorine

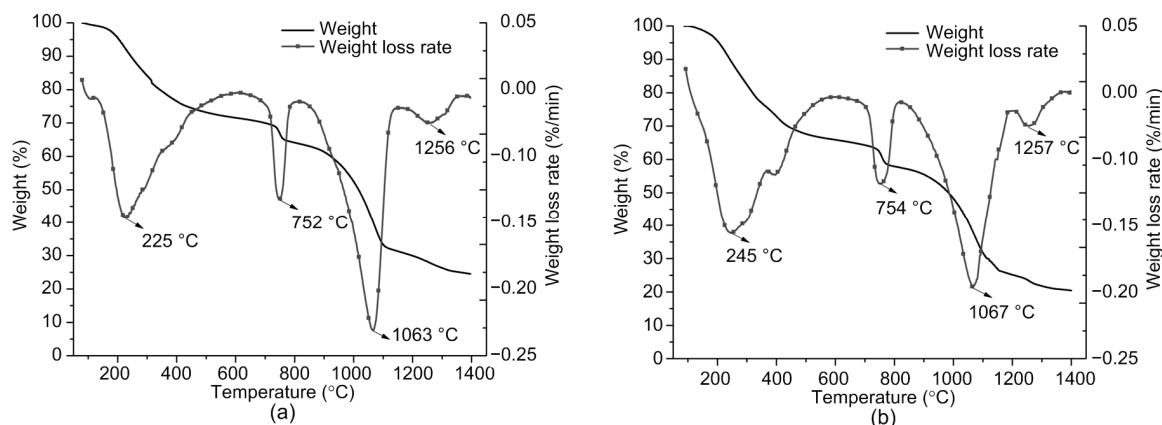


Fig. 4 TG and DTG curves for pyrolysis of the waste of #1 (a) and #2 (b)

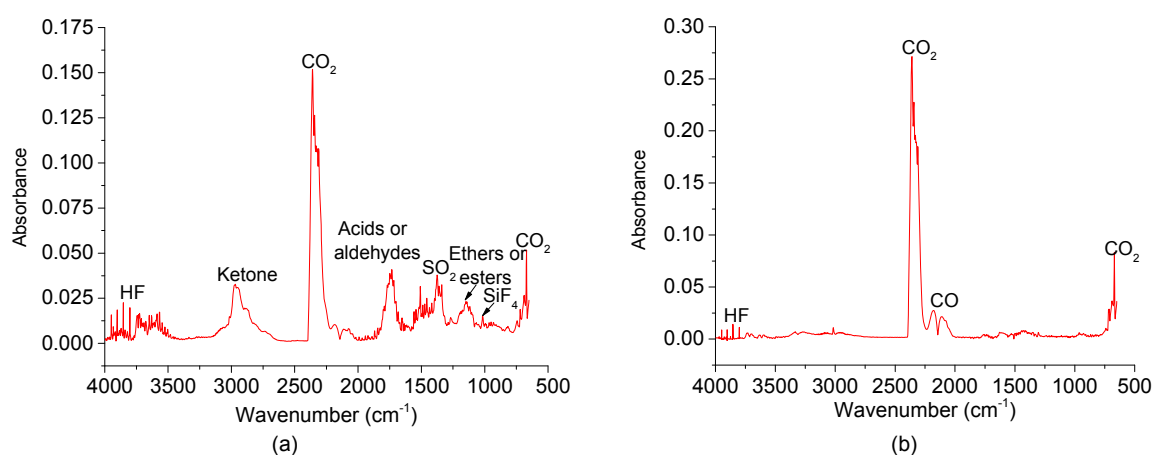


Fig. 5 IR spectrum for pyrolysis products emitted from the waste of #1 (a) 457 °C; (b) 808 °C

coexisting with organic matter was released with the fracture of the hydrocarbon chain (Burgess Jr et al., 1995; Qi et al., 2002). The released fluorine tended to react with activated hydrogen ions in water vapor to generate HF (Liu, 1993). Therefore, the emission of HF in the first stage can not only be caused by the hydrolysis of F⁻ with evaporation of adsorptive and constructive water, but also be due to the decomposition of the organic components. The second stage was from 757.5 °C to 959.6 °C and reached its peak at 812.6 °C. The peak in the second stage was mainly due to the cracking of fixed carbon and further dehydroxylation (Chipera and Bish, 2002). The final stage was from 959.6 °C to the end of the heating process, and the emission of HF increased slowly with rising temperature. This is because the emission of HF in this stage was due to the decomposition of inorganic minerals promoted by the rising temperature,

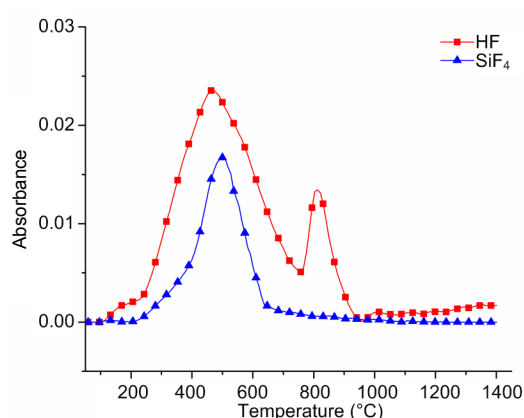
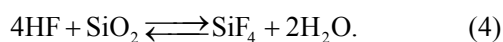


Fig. 6 Evolution of HF and SiF₄ emitted in the pyrolysis process (#1)

which is consistent with the results of previous studies (Li et al., 2005; Guo et al., 2006; Monfort et al., 2008).

HF can corrode SiO₂ in the sample to generate SiF₄, as shown in reaction (4). The emission of SiF₄ started at 132.6 °C and increased with temperature until it reached a peak at 500.2 °C. Then it decreased gradually with rising temperature and almost no SiF₄ was emitted from the sample above 684.0 °C, which is in accord with the results of previous studies (Feng et al., 2012, 2016). It is because the hydrolysis of SiF₄ is an endothermic reaction (Ignatov et al., 2003). The chemical equilibrium of reaction (4) switches to the opposite direction and SiF₄ tends to be hydrolyzed into HF at high temperatures. That indicates that the SiF₄ released from the rotary kiln would be hydrolyzed into HF in the secondary chamber and the burn-out chamber where the temperature was above 1100 °C. Thus, HF was the main form of fluorine gas discharged into the waste heat boiler.



3.2 Concentrations of fluorine in the waste and incineration by-products

The mean concentrations of fluorine in the waste and incineration by-products are presented in Table 5. It is observed that the descending order of fluorine concentration in the incineration residues is: bottom slag, bag filter ash, boiler ash, and burn-out chamber ash. The fluorine concentration in the fly ash (burn-out chamber ash, boiler ash, and bag filter ash) is obviously higher than that in the coal fly ash which is within the broad limits of 0.4–610 mg/kg (Piekos and Paslawska, 1998). The relative enrichment factors (REFs) of fluorine were calculated to illustrate the distribution of fluorine after incineration. The formula is

$$\text{REF} = C_{F, \text{residue}} \times A_{\text{ash in hazardous waste}} / C_{F, \text{hazardous waste}} \quad (5)$$

where $C_{F, \text{residue}}$ and $C_{F, \text{hazardous waste}}$ are the concentrations of fluorine in the residue and hazardous waste, respectively; $A_{\text{ash in hazardous waste}}$ means the ash content in the hazardous waste. REFs in the bottom slag for #1 and #2 were 0.161 and 0.163, respectively, whereas the REFs in the fly ash for #1 and #2 were 0.144 and 0.104, respectively. Qi et al. (2003) suggested that the fluorine in the inorganic minerals would be released

above 800 °C. The outlet temperature of the rotary kiln was approximately 770 °C, as illustrated in Table 2, thus causing incomplete release of fluorine and a large amount of fluorine (12425 mg/kg for #1 and 11605 mg/kg for #2) retained in the bottom slag. Meanwhile, a high calcium content was found in the waste, and previous studies (García-Ten et al., 2006; Monfort et al., 2008; Ponsot et al., 2013) indicated that calcium compounds in the waste would react with the HF in the kiln atmosphere to form CaF₂ below 1000 °C. The outlet temperature of the secondary furnace was about 1170 °C. At that temperature, most of the fluorine would have been released and only a small amount of fluorine, in the complex compounds such as CaF₂-CaO-Al₂O₃ and CaF₂-CaO-SiO₂, whose decomposition temperature is over 1300 °C (Chattopadhyay and Mitchell, 1990; Qi et al., 2003), would remain in the burn-out chamber ash. With a decrease in the flue gas temperature, HF in the flue gas tended to react with oxides in the incineration residues or be adsorbed on residual carbon particles by physical sorption (Piekos and Paslawska, 1999), thus causing enrichment of fluorine in the boiler ash and bag filter ash. The fluorine concentration in the bag filter ash (6725 mg/kg for #1 and 5085 mg/kg for #2) was higher than that in the boiler ash. The difference of fluorine concentration between boiler ash and bag filter ash can be explained by the fact that the flue gas temperature rapidly cooled down to 170 °C at the outlet of the quench tower and this lower temperature promoted the adsorption of fluorine on the bag filter ash. Nitrogen absorption-desorption isotherms of the boiler ash and bag filter ash were obtained in an AUTOSORB-IQ2-MP instrument (Quantachrome, USA) at 77.35 K, as illustrated in Fig. 7. Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) were calculated and found to be quite low, which indicated that the boiler ash and bag filter ash had negligible porosity and the adsorption of fluorine mainly occurred on the exposed surface of the fly ash.

The fluorine concentration in the bag filter ash with the different particle size fractions is illustrated in Fig. 8. It can be seen that the fluorine concentration in the bag filter ash first decreased and then increased with the increase of particle size, which indicated that the fluorine was transferred to the bag filter ash by flue gas entrainment and evaporation-adsorption. The fluorine concentration in the coarse particle fractions

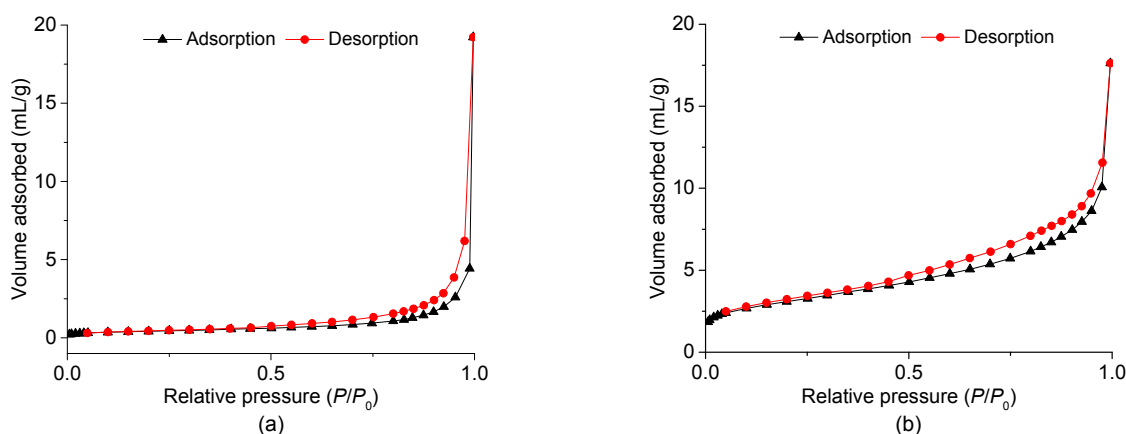


Fig. 7 Adsorption-desorption isotherms of the boiler ash (a) and bag filter ash (b) for #1
(a) $S_{\text{BET}}=1.54 \text{ m}^2/\text{g}$; (b) $S_{\text{BET}}=11.01 \text{ m}^2/\text{g}$

increased with the increase of particle size, which can be explained by the fact that the coarse particles were mainly transmitted into the bag filter ash by entrainment and the fluorine in those coarse particles could not be completely released. The larger the particle size, the more difficult it was for fluorine to be released. The fluorine concentration in the fine particle fractions increased with the decrease of the particle size. This change occurred because the surface area of the fine particles increased as the particle size decreased, thus enhancing their absorptivity for gaseous fluoride.

In addition, the mass distribution of fluorine in the bag filter ash with different particle size fractions was calculated by

$$\omega_{F,i} = c_{F,i} \omega_i / \sum (c_{F,i} \omega_i), \quad (6)$$

where $\omega_{F,i}$ represents the mass distribution of fluorine in a size fraction, and ω_i represents the mass distribution of the size fraction; $c_{F,i}$ is the concentration of fluorine in the size fraction. It was observed in Fig. 9 that the mass distribution of fluorine in the bag filter ash featured a unimodal distribution, and the peak appeared at the size fraction of 106–150 μm .

Particulate fluorine and vapor-phase fluorine in the flue gas were partially absorbed into the absorbent solution of WFGD when the flue gas passed it. The concentrations of fluorine in the absorbent solution and exhaust gas were detected, as noted in Table 5. A high fluorine concentration (88.0 mg/mL for #1 and 69.5 mg/mL for #2) was observed in the absorbent solution, which vastly exceeded the emission limit

Table 5 Mean concentrations of fluorine in the hazardous waste and incineration by-products

Fluorine concentration	Value	
	#1	#2
Hazardous waste (mg/kg)	16 513	13 568
Bottom slag (mg/kg)	12 425	11 605
Burn-out chamber ash (mg/kg)	1398	513
Boiler ash (mg/kg)	2965	1797
Bag filter ash (mg/kg)	6725	5085
Absorbent solution (mg/mL)	88.0	69.5
Exhaust gas (mg/m ³)	4.9	2.9

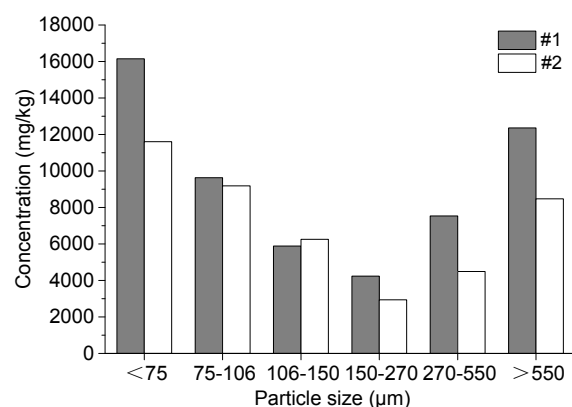


Fig. 8 Fluorine concentration in the bag filter ash with different particle size fractions

(10 mg/L) of the integrated wastewater discharge standard of China (MEE, 1996). The stabilization and removal of fluorine in the absorbent solution is essential to control secondary pollution. The emission of fluorine in the exhaust gas of #1 and #2 met the fluorine emission limit (5 mg/m³) of the Chinese national emission standard (MEE, 2001).

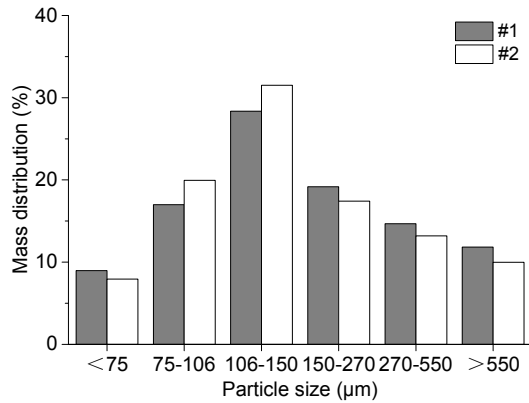


Fig. 9 Mass distribution of fluorine in the bag filter ash with different particle size fractions

3.3 Mass balance and mass distribution of fluorine in the incineration system

The mass balance rate of fluorine in the whole incineration system, which is defined as the ratio of the output to the input amount of fluorine, was calculated to verify the reliability of raw data and expressed as follows:

$$\text{Input}_F = M_{\text{HW}} \times C_{F,\text{HW}}, \quad (7)$$

$$\begin{aligned} \text{Output}_F = & M_{\text{BS}} \times C_{F,\text{BS}} + M_{\text{BCA}} \times C_{F,\text{BCA}} + M_{\text{BA}} \times C_{F,\text{BA}} \\ & + M_{\text{BFA}} \times C_{F,\text{BFA}} + V_{\text{AS}} \times C_{F,\text{AS}} + V_{\text{EG}} \times C_{F,\text{EG}}, \end{aligned} \quad (8)$$

$$\text{Mass balance rate} = \text{Output}_F / \text{Input}_F, \quad (9)$$

where M_{HW} , M_{BS} , M_{BCA} , M_{BA} , M_{BFA} , V_{AS} , and V_{EG} represent the amount of hazardous waste, bottom slag, burn-out chamber ash, boiler ash, bag filter ash, absorbent solution, and exhaust gas, respectively, and are presented in Table 6; C_F represents the concentration of fluorine. The mass balance rates of fluorine for #1 and #2 were 109.45% and 97.63%, respectively, and within the acceptable error range (Reddy et al., 2005; Zhu et al., 2013).

The relative mass distributions of fluorine for #1 and #2 are shown in Figs. 10 and 11, respectively. It was found that fluorine in the hazardous waste had strong volatility and more than 81.69% of fluorine was released into the flue gas. A small amount of fluorine, 16.64% for #1 and 20.73% for #2, was retained in the solid incineration residues. Meanwhile, the fluorine in the bottom slag made up a large pro-

portion of the fluorine in the solid incineration residues. The proportion of fluorine in the burn-out chamber ash, boiler ash, and bag filter ash was quite small and for each less than 1.16%. Most fluorine (83.24% for #1 and 79.17% for #2) was absorbed into the absorbent solution. The proportion of fluorine discharged into the exhaust gas was low, and the proportion was 0.12% for #1 and 0.10% for #2.

Table 6 The amount of hazardous waste, bottom slag, burn-out chamber ash, boiler ash, bag filter ash, absorbent solution, and exhaust gas of #1 and #2

Item	Value	
	#1	#2
Hazardous waste (t)	86.32	93.46
Bottom slag (t)	17.42	19.53
Burn-out chamber ash (t)	7.87	7.58
Boiler ash (t)	5.21	6.51
Bag filter ash (t)	2.49	2.83
Absorbent solution (m ³)	14.76	14.11
Exhaust gas (m ³)	376350	437390

The concentrations of fluorine in the upstream and downstream flue of the WFGD system were also detected, as shown in Table 7. It was observed that the fluorine absorption efficiency of the WFGD system was more than 98%. Particulate fluorine made up a large proportion (98.2% for #1 and 97.3% for #2) of the fluorine in the upstream flue of WFGD system, whereas fluorine primarily existed in the form of vapor-phase fluorine in the downstream flue. The bag filter used in the incineration system had a removal efficiency of over 99% for particulates larger than 10 μm. Meanwhile, the filter used in the sampling had a removal efficiency of more than 99.9% for particulates larger than 0.3 μm. Therefore, it was indicated that most fluorine (98.2% for #1 and 97.3% for #2) remained in the particulates with particle size between 0.3 and 10 μm in the upstream flue of the WFGD system. No particulate fluorine was detected in the downstream flue of the system, demonstrating that it could effectively remove particulate fluorine from the flue gas. Additionally, small droplets of the absorbent solution were entrained in the flue gas and humidity increased significantly in the downstream flue of the WFGD system. It was found that fluorine almost entirely existed in the water vapor or in the droplets in the downstream flue of the WFGD system.

Table 7 Mean concentrations of fluorine in the upstream and downstream flue of the WFGD system

Con- dition	Concentration in upstream flue (mg/m ³)			Concentration in downstream flue (mg/m ³)			
	Particulate fluorine	Vapor-phase fluorine	Total fluorine	Particulate fluorine	Vapor-phase fluorine		Total fluorine
					C _{F,ww}	C _{F,gp}	
#1	192.0	3.5	195.5	ND	2.9	ND	2.9
#2	240.7	6.7	247.4	ND	4.9	ND	4.9

C_{F,ww}: concentration of fluorine in the water vapor or in the droplets; C_{F,gp}: concentration of gaseous-phase fluorine; ND: non-detected

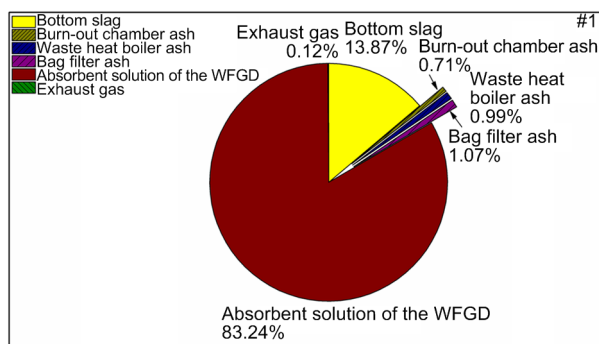


Fig. 10 Relative mass distribution of fluorine in the incineration system for #1

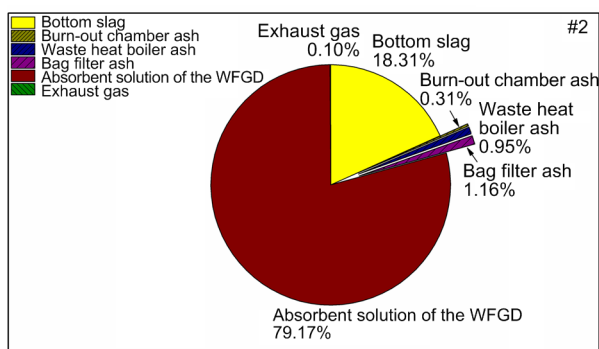


Fig. 11 Relative mass distribution of fluorine in the incineration system for #2

Therefore, a mist eliminator was needed for the further removal of fluorine in the downstream flue of the WFGD system.

3.4 Occurrence of fluorine in the incineration residues

The form of occurrence of fluorine in the incineration residues was investigated using an SCE test. The relative mass proportions of the different forms of fluorine for #1 and #2 are presented in Figs. 12 and 13, respectively. The five studied occurrence forms of fluorine were detected in the bottom slag, in which

fluorine mainly existed in residual form. The existence of organically bound fluorine in the bottom slag indicated incomplete incineration in the rotary kiln. Only residual and acid-soluble fluorine were found in the burn-out chamber ash, which demonstrated that the high temperature in the burn-out chamber promoted the release of water-soluble, exchangeable, and organically bound fluorine. With a decrease in the flue gas temperature, the adsorption of fluorine on the boiler ash and bag filter ash was enhanced. The proportions of water-soluble and exchangeable fluorine in the boiler ash and bag filter ash increased remarkably, especially in respect of the proportion of these two forms of fluorine in the bag filter ash. The proportions of water-soluble, exchangeable, and acid-soluble fluorine in the boiler ash and bag filter ash were both over 80%. Under natural leaching conditions, water-soluble, exchangeable, and acid-soluble fluorine are prone to leaching and cause potential contamination to soil and groundwater. The stabilization and removal of fluorine in the boiler ash and bag filter are therefore needed to control the secondary pollution by the fluorine.

The recovery percentage of fluorine was calculated by

$$\text{Recovery} = (C_{\text{wa},i} + C_{\text{ex},i} + C_{\text{ac},i} + C_{\text{or},i} + C_{\text{re},i}) / C_{\text{F},i}, \quad (10)$$

where $C_{\text{wa},i}$, $C_{\text{ex},i}$, $C_{\text{ac},i}$, $C_{\text{or},i}$, and $C_{\text{re},i}$ represent the concentrations of fluorine in the water-soluble, exchangeable, acid-soluble, organically bound, and residual fraction, respectively; i represents a certain kind of incineration residue; $C_{\text{F},i}$ represents the concentration of fluorine in the incineration residue. It was observed in Figs. 12 and 13 that the recovery percentages of fluorine in the incineration residues were in the range 92.4%–106.3%, which indicated the high reliability of the SCE results.

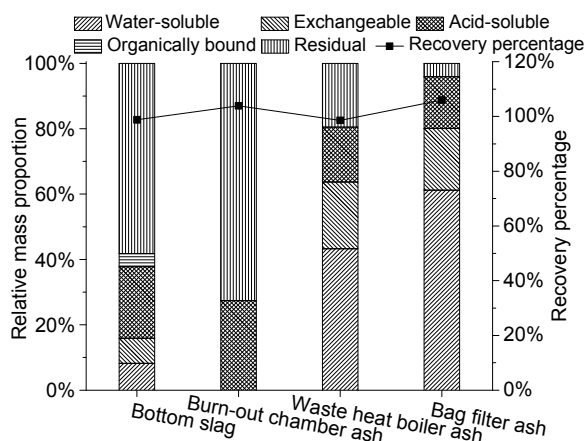


Fig. 12 Relative mass proportion of different occurrence forms of fluorine in the incineration residues of #1

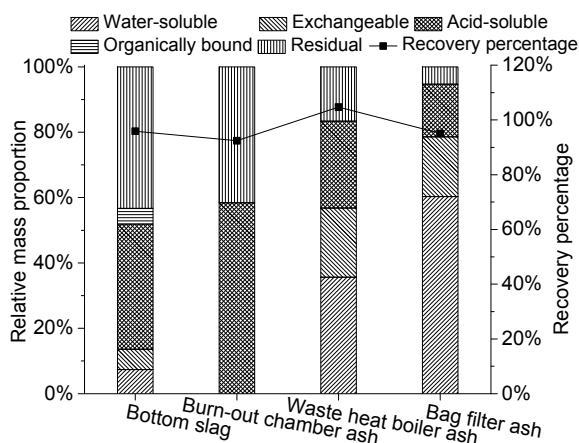


Fig. 13 Relative mass proportion of different occurrence forms of fluorine in the incineration residues of #2

4 Conclusions

The evolution and distribution of fluorine during the incineration of fluorine-containing waste were investigated in a full-scale hazardous waste incinerator. TG-FTIR analysis showed that fluorine in the waste was mainly released in the form of HF and SiF₄ during pyrolysis. The release of HF could be divided into three temperature ranges: 123.5–757.5 °C, 757.5–959.6 °C, and >959.6 °C. The emission of HF in the first stage may be caused by the hydrolysis of F⁻ with evaporation of water and decomposition of organic components. The emission of HF in the second stage was due to the cracking of fixed carbon and further dehydroxylation, while the emission of HF

above 959.6 °C was caused by the decomposition of inorganic minerals. HF can corrode SiO₂ in the sample to form SiF₄. The emission of SiF₄ was mainly concentrated between 132.6 °C and 684.0 °C. SiF₄ tended to be hydrolyzed into HF at high temperatures and almost no SiF₄ was emitted from the sample above 684.0 °C.

Fluorine in the waste had strong volatility and less than 20.73% of the fluorine was retained in the incineration residues. The descending order of fluorine concentration in the incineration residue was as follows: bottom slag, bag filter ash, boiler ash, and burn-out chamber ash. The WFGD system had an absorption efficiency of over 98% for fluorine in the flue gas and a large amount (83.24% for #1 and 79.17% for #2) of fluorine was absorbed into the absorbent solution. The proportion of fluorine discharged into the exhaust gas was below 0.12%. Particulate fluorine made up a large proportion (98.2% for #1 and 97.3% for #2) of the fluorine in the upstream flue of the WFGD system, whereas fluorine in the downstream flue of the WFGD system almost existed in the water vapor or in the droplets.

SCE test results indicated that the five studied occurrence forms of fluorine were detected in the bottom slag. Only residual and acid-soluble fluorine were found in the burn-out chamber ash. High temperature promoted the release of water-soluble, exchangeable, and organically bound fluorine in the burn-out chamber ash. The adsorption of fluorine on the boiler ash and bag filter ash was enhanced as the flue gas temperature decreased, and the proportion of water-soluble and exchangeable fluorine increased. The proportions of water-soluble, exchangeable, and acid-soluble fluorine in the boiler ash and bag filter ash were both over 80%.

Contributors

Wen-han LI did the experiment and wrote the first draft of the manuscript. Zeng-yi MA put forward overarching research methodology and revised the final version. Jian-hua YAN was responsible for coordinating the research activity planning and execution. Qun-xing HUANG and Xu-guang JIANG revised and edited the final version.

Conflict of interest

Wen-han LI, Zeng-yi MA, Jian-hua YAN, Qun-xing HUANG, and Xu-guang JIANG declare that they have no conflict of interest.

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中文概要

题目: 危险废物焚烧炉含氟废物焚烧过程中氟的演化及分布特征

目的: 含氟废物焚烧过程排放的氟化物会危害人体健康, 造成环境污染。本文旨在探究含氟废物焚烧过程中氟的析出特性、氟在焚烧系统中的分布特征以及氟在焚烧灰渣中的赋存形态。这对评估含氟废物在焚烧过程中造成的氟污染以及污染控制具有重要意义。

创新点: 1. 系统研究了氟在焚烧过程中的释放特征以及氟在整个焚烧系统中的质量流, 对评估焚烧过程中的氟污染及污染控制具有重要意义; 2. 系统研究了焚烧灰渣中氟的赋存形态, 为后续灰渣中氟污染控制研究奠定基础。

方法: 1. 采用热重红外联用方法, 分析研究含氟废物热解过程中氟的析出特性(图4和6); 2. 采用高温燃烧水解-离子色谱的方法, 测定焚烧灰渣中的氟含量, 并结合灰渣量等数据, 得到氟在焚烧系统的分布特征(图10和11); 3. 采用连续化学萃取法, 得到焚烧灰渣中氟的赋存形态(图12和13)。

结论: 1. 热解过程中, 含氟废物中氟主要以氟化氢和氟化硅形式释放; 氟化氢的释放可以分为3个温度区: 123.5~757.5 °C、757.5~959.6 °C及959.6 °C以上; 氟化硅的释放主要集中在132.6~684.0 °C。2. 焚烧过程中, 超过79.17%的氟被湿法脱酸系统吸收, 不到20.73%的氟存在于焚烧灰渣中; 排放到大气中的氟占比小于0.12%。3. 底渣和燃尽室灰中的氟主要以残余态存在; 余热锅炉灰和布袋飞灰中水溶态、交换态和酸溶态氟的比例之和均在80%以上。

关键词: 氟污染; 危废焚烧; 含氟废物; 释放特性; 分布特性