research papers

Speciation of zinc in secondary fly ashes of municipal solid waste at high temperatures

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The evaporation aerosols produced during the vitrification process of municipal solid waste incinerators (MSWI) fly ash represent a potential environmental risk owing to their high content of heavy metals. In this research, high-temperature heating processes were carried out on fly ashes collected from bag houses in a Chinese MSWI plant and the secondary fly ashes (SFA) were separately collected at three high temperatures (1273 K, 1423 K and 1523 K) below the melting range. Elemental analysis showed that high contents of both zinc and chlorine were present in these SFA samples and, according to the standard of the heavy metals industrial grade of ore, SFAs can be re-used as metallurgical raw materials or rich ore. Moreover, as shown by XAS analysis and for different high temperatures, zinc environments in the three SFA samples were characterized by the same local structure of the zinc chloride. As a consequence, a zinc recycling procedure can be easily designed based on the configuration information.

Keywords: MSWI; secondary fly ashes; chemical form; XAS; zinc chloride.

1. Introduction

Pollution caused by municipal solid waste incinerators (MSWIs) is becoming a relevant environmental problem and nowadays is an important aspect to be taken into account all over the world. MSWI fly ash is generally classified as hazardous waste and, owing to its high content of heavy metals, e.g. Ni, Cu, Zn, Cd and Pb, has to be carefully monitored and treated prior to disposal (Eighmy et al., 1995; Chan et al., 1996; Kersten et al., 1998; Struis et al., 2004). In the past two decades, much effort has been devoted to investigating and fixing the induced pollution in particular because of the high toxicity of the metal content. At present, China has to face up to the MSWI fly ash problem because, at the end of 2007, 42 MSWIs were in operation in the country with a total designed treatment capacity of ∼13 million tons of waste per year (∼34420 tons per day), producing an estimated amount of fly ash up to a proportion of 3 to 5 wt% of the original waste amount. In addition, it is relevant to consider possible treatments of fly ashes for recycling opportunities for the heavy metals contained as metallurgical raw materials or rich ore.

Although other techniques have been considered, thermal processes are well established as effective treatments of fly ashes (Ludwig et al., 2003). Several approaches, such as cement fixation, acid extraction, vitrification and stabilization with chemical agents, have been considered to solidify or stabilize fly ashes (Sakai & Hiraoka, 2000). Among the existing technologies, vitrification is the most diffused owing to its volume reduction, the weight loss of residues to landfill, the better decomposition of dioxins, the re-use of the molten residue and the reduction of the metal leachability (Boccaccini et al., 1995, 1997; Suzuki et al., 1997). However, owing to their volatility, most of the heavy metals in fly ashes vapourize and reappear in the flue gas during the melting process. They diffuse into the environment representing a high potential risk (Higashi et al., 1996; Takaoka et al., 1997). From the viewpoint of environmental protection and material recycling, the evaporation recovery process of heavy metals in MSWIs has also been considered. In this work, the MSWI fly ash collected in one of the MSWI Chinese plants was heated at three high temperatures (1273 K, 1423 K and 1523 K) which were just below the melting range of this fly ash and supposed to be the most effective temperature range for evaporation behaviour of heavy metals (Jakob et al., 1995); the product collected under these conditions was the secondary fly ash (SFA).

Owing to the high intensity, continuous spectrum, excellent collimation and low emittance, synchrotron radiation sources guarantee a spatial resolution, an accuracy and a signal-to-noise ratio not achievable by any conventional X-ray source. These characteristics are precious for many different analyses in complex systems and for techniques such as X-ray fluorescence, X-ray microdiffraction and X-ray absorption spectroscopy. In this research, X-ray absorption spectroscopy has played a fundamental role in the analysis used to identify the chemical form of zinc in all fly ash samples.

Investigation of samples in this work by both X-ray fluorescence (XRF) and toxicity characteristics leaching procedure (TCLP) methods have only provided information about the heavy metal concentrations but no information about their chemical structures. X-ray diffraction (XRD) also did not provide structural information about zinc, whereas X-ray absorption spectroscopy (XAS) proved to be a reliable technique capable of identifying different Zn species eventually present in SFA samples and returned reliable structural information on the Zn environments. It has been previously applied to the investigation of other hazardous wastes (Struis *et al.*, 2004; Huang *et al.*, 2007; Mansour & Melendres, 1998; O'Day & Carroll, 1998). However, this is the first investigation of real flue gases generated during the heating process. Secondary fly ashes have been collected and analyzed by complementary analytical approaches and with XAS to identify the presence of Zn conformations occurring at different heating temperatures.

2. Experimental section

2.1. Materials and experimental conditions

MSWI fly ash and three secondary fly ashes collected at temperatures of 1273 K, 1423 K and 1523 K were analyzed. The MSWI fly ash was collected from bag houses in a Chinese MSWI plant. The incinerator was fed with about 400 tons per day of raw municipal solid waste. Air pollution control devices containing an adsorption reactor and a fabric filter were also available inside the plant. The MSWI aerosols presented a rounded distribution in the range 38–106 μm. The high-temperature equipment necessary to heat the MSWI fly ash was composed of a furnace made by an Al_2O_3 tube working up to a temperature of 1873 K, a filter bag to collect SFAs and a liquid [5% (v/v) HNO_3 and NaOH] to absorb the end gas.

The chemical composition analyses of all fly ashes were carried out by XRF (PW-2404) and TCLP methods which were performed according to the sulfuric acid and nitric acid (SANA) method, China EPA method HJ/T299-2007, at 296 ± 2 K using an extraction fluid at pH 3.20 ± 0.05. The fluid was prepared by adding 5.0 mL of acetic fluid (H_2SO_4:HNO_3 = 2:1) to 2 L of double-distilled water, diluted to pH 3.20 ± 0.05. Then, 100 g of the sample was placed in a 2 L Erlenmeyer flask, and 1000 mL of extraction fluid was added to each Erlenmeyer flask. Samples were then agitated for 18 h using an electric vibrator. At the end of the extraction, the slurry was filtered using a 0.8 μm pore-size fiberglass filter and the

Table 1
Comparison of the chemical composition of the MSWI fly ash and SFA samples.

	MSWI fly ash	SFA 1273 K	SFA 1423 K	SFA 1523 K
CaO (%)	13.74	0.01	–	0.01
SiO_2 (%)	12.57	0.03	–	0.04
Al_2O_3 (%)	5.39	–	–	0.27
K_2O (%)	9.81	14.59	17.93	15.58
Na_2O (%)	8.52	11.67	14.89	12.87
SO_3 (%)	14.29	–	–	3.63
Cl (%)	18.08	42.15	43.57	39.72
Cu (mg kg^{-1})	11000	44000	37000	57000
Zn (mg kg^{-1})	68000	80000	87000	80000
Pb (mg kg^{-1})	21000	101000	89000	91000
Cd (mg kg^{-1})	1000	3000	3000	2000
Cr (mg kg^{-1})	3000	–	–	–

filtrate liquid was collected to measure the heavy metal concentrations by inductively coupled plasma mass spectrometry (ICP-MS; Finnigan-MAT). Chemical structure information of the MSWI fly ash was obtained by XRD spectroscopy (PW-1700) with Cu $K\alpha$ radiation [5 to 90° (2θ) at a scan rate of 3° min^{-1}]. SFA samples were not measured by XRD owing to their limited available quantities.

2.2. XAS measurements

XAS measurements were performed at the X-ray absorption station of the 1W1B beamline at Beijing Synchrotron Radiation Facility. The typical energy of the storage ring was 2.5 GeV with a current decreasing from 250 to 160 mA when the experiments were running. A Si(111) double-crystal monochromator was used, minimizing the high harmonics content at the Zn K-edge with a detuning of 20% of the two crystals. The absolute energy position was calibrated using a Zn metal foil. The Zn K-edge of Zn powders, ZnS, ZnO, $ZnCl_2$, $ZnSO_4 \cdot 7H_2O$, $3Zn(OH)_2 \cdot 2ZnCO_3 \cdot xH_2O$ and $Zn(OH)_2$ standards were recorded in the transmission mode while samples of MSWI fly ash, SFAs at 1273 K, 1423 K and 1523 K were measured in the fluorescence mode. For the experiments, all standards and samples were ground into fine grains and then well proportioned amounts were distributed on Kapton films. To collect data in transmission, an ion chamber flowed by 25% argon and 75% nitrogen was used to monitor the incident beam intensity (I_0), while a second ion chamber, flowed with the same proportion of argon and nitrogen gas, was used to monitor the beam intensity after the sample (I_1). A Lytle detector flowed by pure Ar was used to record the signal (I_f) in the fluorescence mode. Data analysis of the experimental XAS spectra was performed using the *WinXAS3.1* (Ressler, 1998) and *FEFF8.0* (Ankudinov *et al.*, 1998) packages.

3. Results and discussion

3.1. Component analysis

The components included in the MSWI fly ash and SFAs are summarized in Table 1. The errors in determining the chemical

Table 2
Concentrations of leachable metals in the MSWI fly ash.

	Cu	Zn	Pb	Cd	Cr
SANA concentration (mg L^{-1})	0.05	38.5	1.65	29.0	1.55
Limit (mg L^{-1})	100	100	5.0	1.0	15
Total concentration (mg kg^{-1})	11000	68000	21000	1000	3000
Leachability† (%)	<0.01	0.57	0.08	29.0	0.52

† Leachability = (1000 g/1000 mL)[1000 mL (leachate vol.)/100 g (fly ash)][Cu conc. (leachable)]/(total Cu conc.).

compositions have been estimated to be 5% relative to the content of each element. The content of zinc in the three SFAs showed almost no difference, which was probably caused by the relatively high content of Al_2O_3 and SiO_2 in the MSWI fly ash. The evaporation action of zinc would be improved owing to the existence of Cl, but would be negatively affected by stable chemical formations like $ZnSiO_4$ and $ZnAl_2O_4$ (Jakob *et al.*, 1995, 1996). Moreover, as pointed out by Jakob *et al.*, the evaporation amount of Pb reached an equilibrium at a temperature much lower than 1373 K (the highest temperature monitored below the melting range in their system), while Cu still increased until 1323 K. Finally, both Pb and Cu showed almost complete evaporation, but the evaporation amount of zinc increased so slowly that it was only 50% at 1373 K and did not show any significant increase with temperature above 1373 K (Jakob *et al.*, 1995, 1996). This might explain why the content of Pb and Cu in the SFA samples was higher than those in MSWI fly ash, but the difference in the amount of zinc was not so obvious between the MSWI and SFA samples (Table 1). As for Ca, Si, Al, S and Cr, these were almost non-existent in the SFA samples. Nevertheless, according to the heavy metals industrial grade of ore, the systems analyzed are suitable as metallurgical raw materials or rich ore.

Table 2 shows a comparison of Cu, Zn, Pb, Cd and Cr concentrations in leachates extracted from MSWI fly ash by the SANA test. The estimated Zn leachability is about 0.57%.

XRD results of the MSWI fly ash showed that the major species present were halite, sylvite and gypsum. Additional chemical structural information on Zn was not available owing to the extremely low Zn content and/or its poorly crystalline phases (Struis *et al.*, 2004).

3.2. XANES and EXAFS analysis

XANES data and their corresponding first derivatives of all samples and standards are compared in Fig. 1. Large differences exist among the spectra of the MSWI fly ash and the SFA samples which are almost identical within the signal-to-noise ratio. To compare XANES spectral features we add three vertical dashed lines in Fig. 1(*b*) as guides for the eye. From a qualitative analysis it is clear that the first derivative of the MSWI fly ash is quite similar to that of $ZnCl_2$, $3Zn(OH)_2 \cdot 2ZnCO_3 \cdot xH_2O$ and $ZnSO_4 \cdot 7H_2O$, which may be the main components of the MSWI fly ash. Looking at the SFA spectra, a good correspondence occurs with the first derivative of XANES data of $ZnCl_2$.
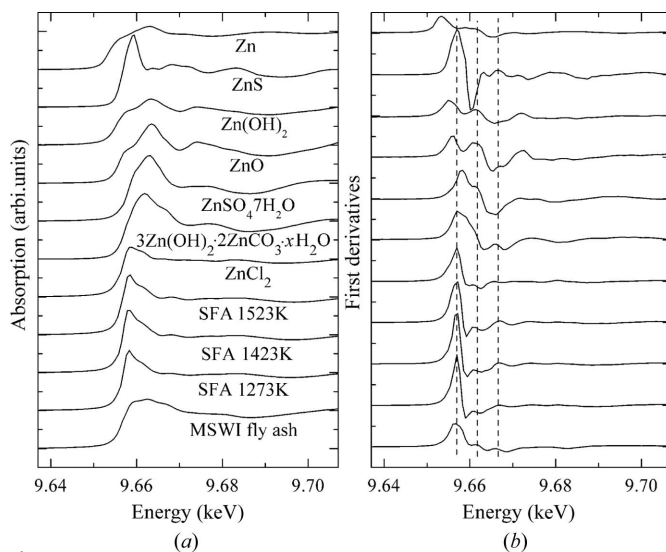

Figure 1
Comparison between XANES spectra of samples and standards: (*a*) Experimental data at the Zn *K*-edge; (*b*) first derivative of the curves of panel (*a*).

LCF (linear combination fit) analysis is a suitable method for evaluating the concentrations of species in complex systems (Roberts *et al.*, 2003) by selecting the possible components from a set of standards. With this method the parameters of standard spectra which do not seem to be contained in the sample will often show negative partial concentrations or unreasonable energy shifts during the fitting process. The residual value (*R*) has been used to evaluate the reliability of the fitting. As shown in different investigations, an error of about 2% in the fitting results corresponds to an uncertainty limit of about 5% (Hsiao *et al.*, 2002, 2006; Takaoka *et al.*, 2005a). The LCF technique of XANES has already been successfully applied to identify and quantify components of fly ashes (Chien *et al.*, 2000; Hsiao *et al.*, 2001a, 2006; Ressler *et al.*, 2000; Takaoka *et al.*, 2005a,b). In this work, we performed LCF analysis using *WinXAS3.1* code in the range −20 to 50 eV around the Zn *K*-absorption edge (*i.e.* 9637–9707 eV). As shown in Fig. 2, from the LCF analysis
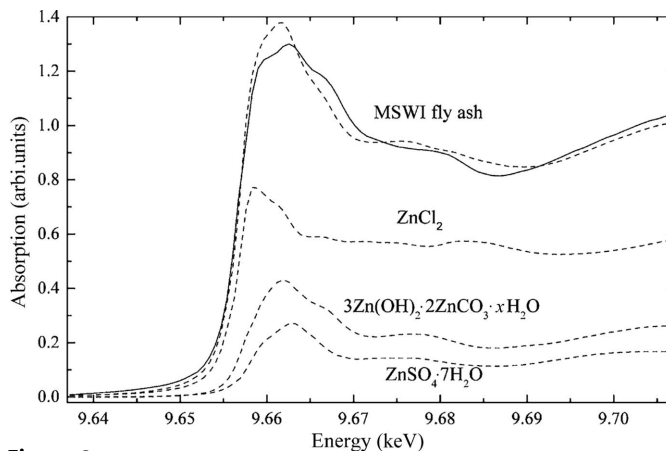

Figure 2
Comparison of the Zn *K*-edge experimental spectrum (solid line), LCF result of the MSWI fly ash sample (top dashed line) and other standards at the Zn *K*-edge.

the main components of the MSWI fly ash are: $ZnCl_2$, $ZnSO_4 \cdot 7H_2O$ and $3Zn(OH)_2 \cdot 2ZnCO_3 \cdot xH_2O$, with relative fractions 0.59, 0.16 and 0.25, respectively, with a residual value $R = 3.6\%$. However, a comparison with the XANES spectrum of willemite (Bazin *et al.*, 2008) clearly suggests that a non-negligible amount of zinc might exist as willemite in the MSWI fly ash. It can probably be used to explain why a better fitting result was not achieved. Besides, a reasonable reconstruction of SFA samples was not achieved either.

Although the LCF analysis of SFA samples at different temperatures was not exhaustive, by taking into account the XANES spectra and their first derivate lines shown in Fig. 1 we clearly recognize the similarity of these spectra with that of $ZnCl_2$. Since the white line of ZnS (Fig. 1) is intense, we may consider it also as one of the species present in the SFA samples. However, the chemical analysis as summarized in Table 1 does not support the presence of sulfur in the three SFA samples and, as shown in Fig. 3, the EXAFS signals of the first coordination shells of the SFA samples are also consistent with the presence of $ZnCl_2$, a condition that implies a similar local structure around zinc ions. Indeed, we observe only a small amplitude reduction of the SFA sample at 1273 K while the other two samples exhibit the same EXAFS amplitude and frequency.

To improve the structural reconstruction of SFA samples and to identify differences among them, we fit EXAFS oscillations using *WinXAS3.1* code (Ressler, 1998) and theoretical models generated by *FEFF8.0* (Ankudinov *et al.*, 1998). Indeed, the EXAFS analysis has already been applied to the structural characterization of hazardous wastes (Hsiao *et al.*, 2001b; Manceau *et al.*, 1996) and has provided information on coordination species, accurate bond distances (R) and coordination numbers (CN) (Hsiao *et al.*, 2002; Lin & Wang, 2000). The Fourier transform of each spectrum was performed on the k^3-weighted EXAFS oscillations in the range 3.2–11.2 Å^{-1}. The amplitude reduction factor (S_0^2) was set to 0.9 and the error for bond distance was estimated to be about 0.02 Å and
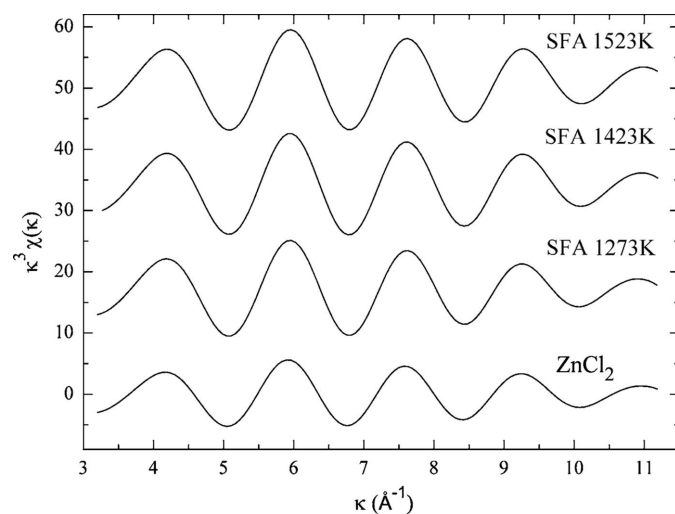
Table 3
EXAFS parameters around the Zn ion in $ZnCl_2$ and in three SFA samples.

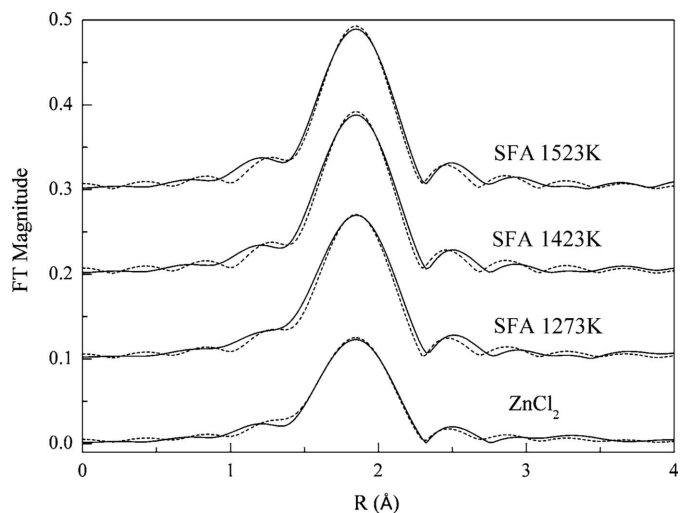| Samples	CN	R (Å)	σ^2 (Å^2)	R (%)
$ZnCl_2$	3.6	2.27	0.0080	5.5
SFA 1273 K	4.2	2.27	0.0063	6.6
SFA 1423 K	4.2	2.27	0.0054	6.7
SFA 1523 K	4.2	2.27	0.0054	6.1

Figure 4
Comparison of the fits of the Fourier transform (dots) of the EXAFS spectra (line) of the three SFA samples and of $ZnCl_2$.

for the coordination number was within 20% (Struis *et al.*, 2004; Ford & Sparks, 2000). In the real space the main intense peak of each spectrum (R space, 0.9–2.3 Å) corresponds to the contribution of chloride atoms. Results are summarized in Table 3 and shown in Fig. 4.

The distance of the Zn—Cl bond obtained by the fit is 2.27 Å, a value consistent with the structure of $ZnCl_2$. Moreover, from Table 3, it is also evident that the coordination numbers of SFA samples are similar to that of $ZnCl_2$, but the σ^2 values are smaller than that of $ZnCl_2$. The Debye–Waller factor of the SFA 1273 K sample is the highest among the three SFAs, consistent with the observed EXAFS amplitudes. Although this phenomenon needs further investigations, it is probably due to the coexistence of different ordered structures or variation of particle sizes inside the SFA samples. However, the similarity between structural parameters of SFA samples is in agreement with the XANES data. Both XANES and EXAFS results at the Zn K-edge indicate that Zn is present with almost the same identical chemical form at the three high temperatures.

4. Conclusions

To summarize, according to the results of the component analysis we may claim that SFA samples collected at high temperatures (1273 K, 1423 K and 1523 K) can be treated as metallurgical raw materials or rich ore. Moreover, both qualitative and quantitative XAS analyses showed that zinc

Figure 3
Comparison of EXAFS spectra of the first coordination shells among $ZnCl_2$ and the three SFA samples.

ions in SFAs were all coordinated with chlorine atoms and existed in an almost identical chemical form with the temperature rising. As a consequence, an almost 'pure' Zn configuration occurred in collected SFA samples. This result confirmed the influence of chloride on the evaporation by XAFS. If confirmed by more systematic investigations, this work will make a possible basis for setting up a unique Zn recycling process extremely useful for avoiding or minimizing pollution generated during MSWI operations and fly ash productions.

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