A study on the chemical and mineralogical characterization of MSWI fly ash using a sequential extraction procedure

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Abstract

The presence of heavy metals in municipal solid waste incineration (MSWI) fly ash is of environmental concern due to their leaching potential in landfill environments. Sequential chemical extraction was performed on fly ash samples from a large-scale municipal solid waste incineration plant in East China. The transformation of the mineralogical species of fly ash during the sequential extraction was studied using X-ray fluorescence (XRF) and X-ray powder diffraction (XRD). The leaching behavior of heavy metals such as zinc, lead, cadmium and copper in MSWI fly ash was considered to have a dependency relationship with the components of calcium, such as aphthitalite, calcite, anhydrite and calcium aluminate or calcium aluminosilicate.

1. Introduction

Over the past two decades, the treatment of municipal solid waste by incineration has been adopted gradually in China, with the advantages of reducing solid waste volume by up to 90% and of providing heat to make electricity or steam. The total treatment capacity of MSW incineration facilities in service was about 13,000 t per day by 2002, and is expected to reach around 48,000 t per day in 2010. In many big cities, incineration has been the major treatment mode for MSW [1]. Worldwide tightened environmental standards have improved air pollution control system for flue gas, and more efficient separation technologies have increased the amount and pollution potential of fly ash (the solid captured in the gas stream). In many countries, fly ash are classified as hazardous wastes, and therefore require special handling [2]. Most fly ash from MSW incineration goes to landfill in China, so the leaching of the heavy metals from the fly ash by water in landfill environments has received considerable attention and has been addressed in previous literature [1].

Fly ash from MSW incineration (MSWI) is a complex mixture of various minerals. Spherical particles are common in fly ash, associated with aggregates of polycrystalline, amorphous and glassy material [3–5]. The spherical particles are composed of complex calcium, sodium and potassium aluminosilicates whilst the associated amorphous and crystalline material is enriched in the more volatile heavy metals [3]. In such a complex system, the leachability of heavy metals is complicated and confusing because of the difficulty of identifying the exact chemical species of the heavy metals.

A sequential chemical extraction (SCE) procedure proposed by Tessier [6] has been widely used to investigate the chemical phases of heavy metals in fly ash. In Tessier's procedure, he classified five chemical types of ions to bind on the surface of an inorganic matrix: exchangeable phase, carbonates phase, Fe–Mn oxides, organic matter phase and residual (silicates) phase. The International Ash Working Group (IAWG) [2] concluded that the results of sequential extraction might not necessarily reflect the associations with the claimed phases, but rather represent the different leaching conditions within a landfill over time. The exchangeable phase is immediately available under neutral conditions; the carbonates phase is potentially available under neutral conditions; the phases of Fe–Mn oxides and organic matter are potentially available under reducing conditions; the residual phase is unavailable for leaching.

In this paper, the transformation of the mineralogical species of fly ash and the leachability of major components and heavy metals during sequential extraction will be investigated, in or-

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der to understand the relationship between the leachability of heavy metals and the mineralogical characterization of MSWI fly ash.

2. Materials and methods

2.1. Sampling

We sampled from a large-scale MSW incineration plant in East China, which had three sets of 350 t per day scale stoker furnace. The furnaces operate at about 900 °C. In each furnace, a semi-dry lime scrubbing system and fabric bag filter precipitator is applied. Fly ash is collected after the flue gas is cooling to less than 150 °C. Fly ash used in this paper was sampled from the ash exhaust of the fabric bag filter precipitator. All the samples were sieved by an auto sieve (Retch contol-g-200, Germany) and the coarse fraction (particle size > 500 μm) was discarded.

2.2. Fly ash composition analysis

The major constituents in the ash are Si, Ca, S, Al, Cl, K, Na, Fe, Mg, P and so on, plus oxygen as the most prominent element in the form of oxides, silicates and aluminosilicates. There are also a large range of trace elements, including Pb, Zn, Cu, Cr, Ni, Cd, Ag, As, and other heavy metals. Major elements analysis of fly ash was performed by using an X-ray fluorescence spectrometer (XRF, Shimadzu Lab Center XRF-1700, Japan). The concentrations of individual trace elements in the fly ash were analyzed after the sample was digested according to an ASTM method [7], which is used for coal and coal fly ash primely and introduced to digest MSWI fly ash recently [8]. Approximately 0.5000 g of the thoroughly blended ash sample was accurately weighed into a 100 mL Teflon beaker. Twenty millilitres of aqua regia (HNO_3 : HCl = 1 : 3) and 20 mL of concentrated hydrofluoric acid were added to the beaker. Then, the beaker was placed on a hot plate that had been adjusted to 130–150 °C. After the solution was evaporated to near dryness, the beaker walls were rinsed with deionized water and this solution was heated to dryness. One millilitre of concentrated nitric acid and a further 20 mL of deionized water were added after the beaker was removed from the hot plate and cooled to room temperature. The beaker was heated again on a hot plate at 90–100 °C, most of the sample being digested into solution after 1 h. Cooled to room temperature, the solution was filtered and then diluted to volume with deionized water in a 100 mL volumetric flask. The element concentrations in the solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer Elan 6000, USA).

2.3. Sequential extraction

Normally, the sequential chemical extraction suggested by Tessier [6] is to be performed in a 150 mL beaker flask on duplicated sample according to the following procedure:

Exchangeable (F_1): 5.0 g of fly ash sample is added with 100 mL of 1 mol L^{-1} sodium acetate (CH_3COONa) at pH 8.2 and shaken for 1 h at room temperature;

Bound to carbonate (F_2): The residue from the exchangeable fraction is shaken with 100 mL of 1 mol L^{-1} CH_3COONa at pH 5.0 (adjusted with CH_3COOH) for 5 h at room temperature;

Bound to Fe–Mn oxides (F_3): 100 mL of 0.04 mol L^{-1} hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 25% (v/v) CH_3COOH is added to the residue from the carbonate fraction and heated at 96 ± 3 °C for 5 h with occasional agitation;

Bound to organic matters (F_4): 15 mL of 0.02 mol L^{-1} HNO_3 and 25 mL of 30% hydrogen peroxide (H_2O_2) (pH 2 adjusted with HNO_3) are added to the residue from the Fe–Mn oxides fraction and heated at 85 ± 2 °C for 2 h with occasional agitation. Another aliquot of 15 mL 30% hydrogen peroxide (H_2O_2) (pH 2 adjusted with HNO_3) is added and heated again at 85 ± 2 °C for 3 h with intermittent agitation. After cooling to room temperature, 25 mL of 3.2 mol L^{-1} ammonium acetate (CH_3COONH_4) in 20% HNO_3 is added and the sample is diluted to 100 mL and agitated continuously for 30 min;

Residual fraction (F_5): The residual fraction is determined by digestion of 0.5 g (dry weight) of residue from the fraction bound to organic matters, with aqua regia and concentrated hydrofluoric acid, according to the procedure described in Section 2.2.

After each extraction, the separation is achieved by centrifuging at 3000 rpm for 20 min and the supernatant is filtered through 0.45 μm membranes. The trace element concentrations in the supernatant are finally determined by ICP-MS.

Nevertheless, in the work of this study, the contents of major elements and heavy metals in fly ash occur together at the same time, while it is inconvenient to determine them together by ICP-MS because of the large difference between their concentrations. So, a method which can determine both major elements and heavy metals was sought. Takaoka et al. [9] evaluated the validity of XRF analysis to the determination of elements in fly ash by comparing measured values from three analysis methods: XRF, inductively coupled plasma atomic emission spectrometry (ICP-AES) and neutron activation analysis (NAA). They concluded that XRF analysis is applicable for most elements in fly ash, with very few exceptions such as arsenic, cadmium, mercury, silver and so on. Therefore, XRF analysis was adopted in our study.

Four duplicated fly ash samples were each extracted to their exchangeable fraction, carbonate fraction, Fe–Mn oxides fraction and organic matters fraction. The residues from the four fractions, named, respectively, R_1, R_2, R_3 and R_4, were dried at 105 °C for 24 h and then analyzed by XRF.

Mineralogical investigations of these residue samples (R_1 to R_4) were carried out by X-ray powder diffraction (XRD, Rigaku D/max-r B, Japan). The setting conditions for the XRD were: Cu Kα radiation, 40 keV accelerating voltage, 80 mA current, 10–70°2θ scanning range, 0.02° step and 6 °/min scan speed.

Table 1
The content of trace elements in MSWI fly ash (mg kg^{-1})

Elements	Value
Zn	6089.93
Sn	5879.51
Pb	4769.96
Mn	2034.66
Cu	976.74
Cr	318.43
Ni	185.67
As	82.43
Cd	72.02
Co	36.94
Ag	11.75
Hg	N.D.

3. Results and discussions

3.1. Fly ash composition

Table 1 shows the trace elements of the MSWI fly ash samples determined by ICP-MS and the first column of Table 2 gives the major components determined by XRF. The fly ash contained large amounts of SiO_2 (23.64%), CaO (22.78%), SO_3 (13.99%), Al_2O_3 (8.18%), Cl (6.40%), K_2O (5.60%) and Na_2O (5.28%) while the content of other oxides was less than 5%. The major heavy metals identified in the fly ash were Zn, Sn, Pb, Mn and Cu.

3.2. Leaching of major components and transformation of mineralogical species during SCE

The composition of the untreated fly ash and the residues from sequential extraction, in percentage by weight, are compared in Table 2. A ternary diagram[10] as shown in Fig. 1 gives the variation of the main components (SiO_2, CaO and Al_2O_3) during sequential extraction. Because SiO_2 was hardly degraded in the first four steps (F_1 to F_4) of the sequential extraction, the content

Table 2
XRF analysis on untreated fly ash and the residues from SCE (wt.%)

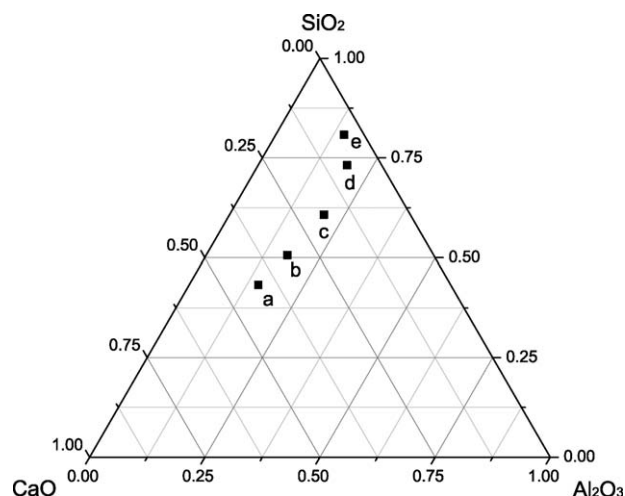| Components	Untreated fly ash	Residues from SCE			
		R_1	R_2	R_3	R_4
SiO_2	23.64	35.47	46.96	57.05	65.69
CaO	22.78	22.23	14.51	5.84	3.55
SO_3	13.99	5.59	0.52	0.34	0.20
Al_2O_3	8.18	12.34	15.83	15.07	12.01
Cl	6.40	0.58	0.25	0.16	0.00
K_2O	5.60	2.39	3.14	2.40	2.66
Na_2O	5.28	2.31	0.21	0.92	0.73
Fe_2O_3	4.83	5.88	7.61	6.70	7.16
MgO	2.64	4.11	0.28	1.22	1.72
P_2O_5	2.49	4.16	5.37	5.43	1.53
TiO_2	1.36	1.64	2.15	2.36	2.39
ZnO	0.93	1.13	1.06	0.72	0.76
PbO	0.55	0.57	0.35	0.24	0.13
SnO_2	0.44	0.57	0.73	0.83	0.83
MnO	0.27	0.37	0.39	0.18	0.17
Cr_2O_3	0.15	0.17	0.19	0.19	0.18
CuO	0.14	0.16	0.10	0.06	0.05
Others	0.32	0.32	0.35	0.31	0.24

Fig. 1. Ternary diagram of XRF analysis on untreated fly ash and the residues from SCE. (a) untreated fly ash, (b) residue from exchangeable fraction, (c) residue from carbonate fraction, (d) residue from Fe–Mn oxides fraction, (e) residue from organic matters fraction.

ratio of SiO_2 showed an increasing tendency. The content ratio of Al_2O_3 was approximately constant while the content ratio of CaO showed a decreasing tendency. This indicates that the degradation of the compounds of calcium was more dependent on the condition of sequential extraction than the compounds of aluminum; in other words, the compounds of calcium could be regarded as an indicator of the progress of the sequential extraction. Therefore, the values in Table 2 were normalized by dividing them by the content ratio of SiO_2. The relationship between the absolute content ratios of sulfur, chlorine and aluminium versus calcium, respectively, is shown in Fig. 2.

The result of powder diffraction analysis on untreated fly ash and the residues from sequential extraction was shown in Fig. 3. The characteristic peaks of SiO_2 were obvious in each curve. Other characteristic peaks, which were more difficult to identify, also survived the sequential extraction. However, it was the transformed mineralogical species which really concerned us
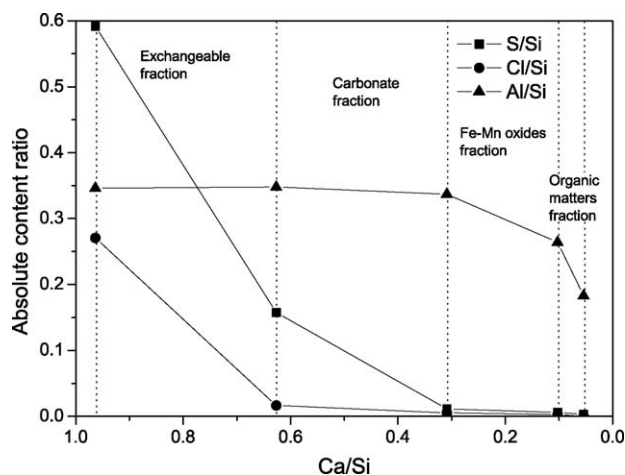

Fig. 2. The relationship between the absolute content ratio of S, Cl and Al vs. Ca, respectively.
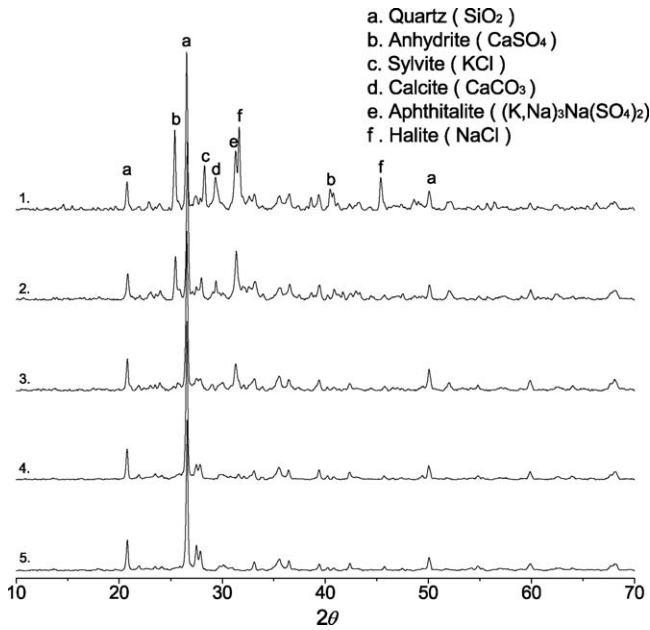
Fig. 3. XRD analysis on untreated fly ash and the residues from SCE. ((1) untreated fly ash, (2) residue from exchangeable fraction, (3) residue from carbonate fraction, (4) residue from Fe–Mn oxides fraction, (5) residue from organic matters fraction.)

Fig. 4. The relationship between the absolute content ratio of heavy metals versus calcium respectively.

here. By associating the power diffraction data with the variety progression of the absolute content ratios of the major components (in the untreated fly ash and its residues from sequential extraction), these transformed mineralogical species were tentatively identified.

The characteristic peaks of sylvite (Fig. 3c) and halite (Fig. 3f) disappeared in the XRD curve of the residue from the exchangeable fraction. At the same time, most of the chlorine was consumed during the exchangeable fraction, as shown in Fig. 2. The characteristic peaks of aphthitalite (e in Fig. 3) faded away gradually in the XRD curve of the residue from both exchangeable fraction and carbonate fraction. This was consistent with the tendency to consume sulfur in Fig. 2. The characteristic peaks of anhydrite (Fig. 3b) and calcite (Fig. 3d) were not obvious in the XRD curve of the residue from the carbonate fraction, while the content ratio of CaO continuously decreased as shown in Fig. 1. This indicates that some compounds of calcium in an amorphous state, which could not be detected in the XRD curve, were degraded in the last three steps of sequential extraction (F_3 to F_5). On the other hand, with the decrease of the ratio of calcium to silica, the absolute content ratio of aluminum remained constant in the first two steps (F_1 to F_2) and began to decrease at the third step (F_3) of sequential extraction, as shown in Fig. 2. It was thus to be expected that the compounds of calcium in amorphous substance would be calcium aluminate or calcium aluminosilicate.

3.3. Leaching of heavy metals during SCE

The variety of the contents of heavy metals during the sequential extraction is shown in Fig. 4, in which the absolute content
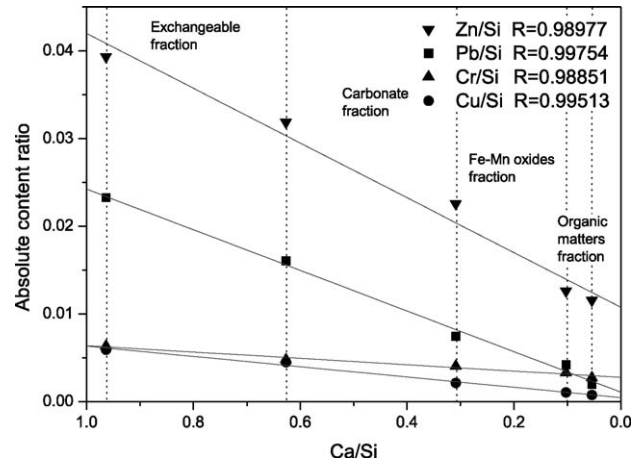
ratio of zinc, lead, chromium and copper, respectively, are seen to be linear with that of calcium, with a decreasing tendency. Obviously, the decreasing tendency of lead and zinc was much greater than of chromium and copper. At the same time, about half of the lead and zinc had been released after the first two steps (F_1 and F_2) of sequential extraction. This indicates that lead and zinc in MSWI fly ash have a high leaching potential, and would release easily in a leaching landfill.

The linear relationship, between the absolute content ratio of heavy metals and of calcium, hinted that the degradation of the compounds of calcium could give some clue about the release of heavy metals. Aphthitalite, calcite and anhydrite in the first two steps (F_1 and F_2) of the sequential extraction, and the amorphous substance of calcium, such as calcium aluminate and calcium aluminosilicate, in the subsequent steps, are thought to have played an important role. Ordinary physical and chemical adsorption could be regarded as the most important relationship between heavy metals and aphthitalite, calcite and anhydtite. This relationship was rarely stable, while the metal aluminium silicate was stable because of its complex formation mechanism, as detailed by Wu et al. [11]. They suggest that the formation process consists of adsorption of the metal followed by diffusion in the product layer (which consists of a molten metalaluminosilicate) and finally reaction with the aluminosilicate matrix.

4. Conclusions

We have elucidated the transformation of the mineralogical species and leachability of major components and heavy metals in MSWI fly ash during a sequential extraction. The leaching behavior of heavy metals was found to have a dependency relationship with the components of calcium. Heavy metals bonded to the exchangeable fraction or the carbonates fraction (which was considered easily available under neutral conditions), associated with aphthitalite, calcite and anhydrite by ordinary physical and chemical adsorption. The heavy metals reacted with the aluminosilicate matrix of fly ash were difficult to leach under neutral conditions and potential available under reducing condi-

tions. They were present as bonding to Fe–Mn oxides fraction or organic matter fraction in the sequential extraction.

Acknowledgements

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