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Research article

Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior

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ABSTRACT

This study aims to identify the chemical species and leaching behavior of Cd, Zn, Pb, Cu and Cr in a fly ash with high content of calcium collected from the incineration of municipal solid waste (MWS), based on the sequential leaching procedure. A thermodynamic pseudo-equilibrium model was also developed to evaluate the possible chemical compounds of these heavy metals in the fly ash. The results indicate that, approximate 30% of Cu was distributed in the organic bound fraction and very likely combined with some organic ligands. Pb exhibited the highest fraction among these five metals in water soluble fraction, accounting for about 7.5%. It thus potentially causes a menace to the surroundings. In terms of model calculation, the metallic chlorides in the fly ash were responsible for the leaching of Pb, Zn, Cd and Cu even under a rigorous environmental condition (pH = 2) where the oxides and/or metallic ferrites were rarely mobile. The leaching of Cr and Cd in the fly ash was controlled by a dissolution mechanism whereas the fate of Pb, Zn and Cu was controlled by the precipitation/sorption. Cu and Zn in fly ash have been proven to associate with Ca-bearing compounds through precipitation/sorption during leaching test while Pb mainly exists as sulfate and phosphate.

1. Introduction

Incineration processes are commonly employed for the treatment of municipal solid waste (MSW) due to its advantage of mass and volume reduction, energy recovery and hazardous components sterilization [1,2]. However, in comparison to the combustion residues from other solid fuels (e.g. coal and biomass), the content of heavy metals in MSWI ashes is several times higher, raising a challenge for handling with such residues through landfill due to the possibility of the dissolution of water-soluble species into the ecosystem. Therefore, it is urgent to elucidate the mobilization mechanisms of heavy metals and control their leaching to minimize the adverse impact on the environment.

Plenty of research works have been conducted to examine the release of heavy metals from incineration ash [3–7]. In general, the leaching behavior of heavy metals is dependent on the bulk properties of hosting particles, their mode of occurrence and pH of the leaching solution [7]. In contrast to coarse ash particles, fine particulates with a large specific surface area readily expose to solution and in turn cause a great amount of metals to release through surface contact in a short-term leaching. Nevertheless, decrease in the particle size promotes the adsorption of heavy metals due to more available mineral surfaces [4]. The major elements including Si, Al, Ca and Fe directly affect the ash properties (acid or alkaline) and the mineralogical composition, which play a key role on the leaching of toxic heavy metals [2]. Under an acidic condition, the heavy metals are drastically leached out, which, however, could be prevented under alkaline condition through precipitation and/or sorption [8]. This varying tendency from acidic condition to alkaline condition is not monotonous, and highly depends on the property of metallic compounds such as cationic, amphoteric and oxyanionic elements [9,10].

In order to control the emission of acid gases such as HCl and SO_x, calcium-containing compounds (e.g. $CaCO_3$) are usually injected into furnace as an adsorbent during the incineration of MSW [11,12], which hence results in high calcium content in solid residues and in turn changes the ash properties. Although the heavy metals are preferentially mobile under acid conditions, the strong alkaline condition potentially triggers the release of heavy metals particularly for amphoteric elements such as Pb and Zn. Therefore, considerable attentions should be paid to the mobility of toxic heavy metals in the incineration ash with high content of calcium. The existence of high content of calcium in the fly ash during leaching probably promotes the competition between the adsorption and dissolution of heavy metals, thereby altering the leaching behavior of heavy metals. The roles of calcium on the leaching behavior of heavy metals are however not fully addressed.

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Chemical species of heavy metals in ash is influential on their leaching behavior. For instance, metallic chlorides and/or sulfates condensed on the ash particle surface are prone to mobilize due to their high solubility in neutral solution whereas the metals associated with silicates are relatively stable. Hence, understanding the possible chemical species of heavy metals in fly ash is significant to reveal their leaching mechanisms. Prediction based on the thermodynamic equilibrium perspective is one of the simple and convenient methods to reveal the chemical species of heavy metals in MSW ash. However, the results from thermodynamic equilibrium are normally inconsistent with that of real ash since of the short residence time, flue gas cooling rate and kinetic control in the incineration zone and flue gas cooling stage [13]. In this study, a thermodynamic pseudo-equilibrium model was firstly developed using ChemApp linked with the database of FactSage 7.0 for the prediction of metallic species in fly ash so as to systematically investigate the leaching behavior of five heavy metals (Cu, Zn, Pb, Cd and Cr) in MSW fly ash. The model calculation was carried out in terms of the fly ash yield and the fraction of residual from sequential leaching test. A sequential leaching procedure was employed to determine the chemical fractions of each metal in the fly ash [14,15]. A pH-dependent leaching was subsequently conducted to clarify the potential leaching behavior of each metal with the shift of environmental conditions. Finally, the leaching mechanisms of each metal were elucidated through the time-dependent leaching.

2. Experimental

2.1. Properties of fly ash sample

A fly ash sample was collected from a MSW incineration plant in Aichi-ken of Japan, where a stoker furnace was used. The collected ash were dried at 105 °C in an oven for moisture removal, then milled until the ash can completely pass through the sieve with a cut-off size of 100 μm prior to its use. The moisture content in fly ash dropped to 1.4 *wt%*. The composition of major elements in the fly ash is listed in Table 1. Calcium and chlorine are the two dominant elements, accounting for 53.7 *wt%* and 22 *wt%*, respectively. XRD analysis in Fig. 1 suggests that the primary Ca-bearing minerals are $CaCO_3$, CaClOH and $CaSO_4$ while the chlorine in the ash sample is attributed to a great quantity of CaClOH, KCl and NaCl. Si, Al and Fe in this fly ash sample is deficient, accounting to 7.5 *wt%* in total. Table 2 shows the concentration of heavy metals of Cd, Cu, Zn, Pb and Cr in the ash sample. The average concentration of each metal from Ref. [16] was also listed here for comparison. The concentrations of target heavy metals in the ash sample tested in this study were lower than that reported from the literature, indicative of low toxic properties of the fly ash sample to be tested hereafter.

2.2. Sequential leaching procedure

The chemical fractions of each metal in the fly ash sample were determined according to a sequential leaching procedure [14,15]. The procedure used in this study divided each metal into six fractions: F1-water soluble fraction; F2-exchangable fraction; F3-bound to carbonates; F4-bound to Fe-Mn oxides; F5-bound to organic matter and F6-residual. The detailed sequential leaching procedure and parameters are tabulated in Table 3. In brief, the ash of 5 g was employed for initial step. The slurry generated from each step was subjected to a vacuum filtration with a membrane filter (0.45 μm, Millipore) and then washed using deionized water before next leaching step. The resulting leachate from each step was, if necessary, acidized using a few of HNO_3 before ICP-OES analysis.

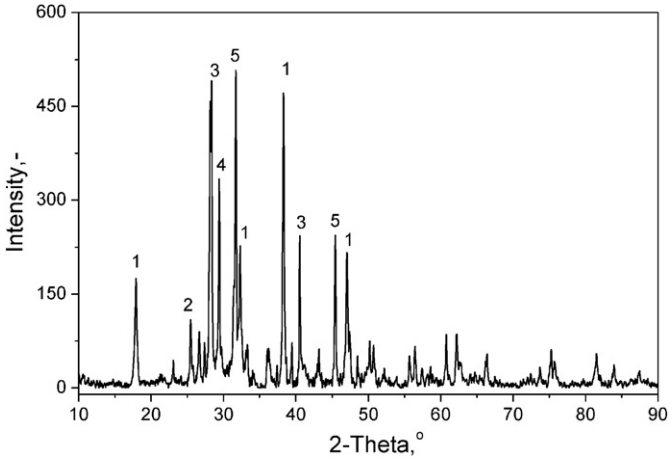

Fig. 1. XRD spectrum of fly ash. 1-Calcium chloride hydroxide (CaClOH); 2-Anhydrite ($CaSO_4$); 3-Potassium chloride (KCl); 4-Calcium carbonate ($CaCO_3$); 5-Sodium chloride (NaCl).

2.3. pH-dependent leaching

The pH-dependent leaching experiments under a wide range pH from 2 to 14 were performed using a method suggested by van der Sloot et al. [17] with some revisions. Generally, the ash of 10 g was initially mixed with about 60 mL deionized water, and then the solution of 10 M HNO_3 or 10 M NaOH was dropped into slurry to adjust the pH to target value. Another portion of deionized water was then added into the slurry to match the liquid/solid ratio of around 9. The resulting slurry sample was stirred for 6 h at room temperature, using a magnetic stirrer (AS ONE REXIM RS-6DR) at a rotatory rate of (200 ± 10) rpm. The pH was controlled continuously during leaching, through the dropping of 0.5 M HNO_3 or 0.1 M NaOH automatically by a pH controller (TOADKK HM-30R). The final liquid to solid ratio was about 10 ± 0.5 (mL g^{-1}).

2.4. Characterization

Heavy metals in the ash sample were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Seiko SPS7000). Prior to analysis, acid digestion of ash samples was conducted in a microwave oven (Milestone Ethos D) based on a procedure with

Table 1
Concentration of major elements in fly ash and bottom ash.

Elements	Fly ash, *wt%*	Bottom ash, *wt%*
SiO_2	3.80	27.9
Al_2O_3	2.54	7.99
Fe_2O_3	1.12	6.60
CaO	53.7	40.7
MgO	1.09	2.53
K_2O	3.31	1.59
Na_2O	5.42	4.62
TiO_2	0.72	1.43
P_2O_5	0.67	3.53
SO_3	4.18	0.48
Cl	22.0	1.52

Table 2
Concentration of heavy metals in the fly ash and bottom ash, as well as the average concentration of each metal from literature. The number in each bracket denotes the number of stokers.

Elements	Fly ash, mg/kg		Bottom ash, mg/kg	
	This study	Literature	This study	Literature
Cd	57.3 ± 0.20	124 (52)	14.90 ± 1.1	15 (77)
Cu	423.6 ± 2.1	1232 (49)	1770 ± 27	2818 (86)
Zn	6394 ± 38	15,848 (62)	2901 ± 1.1	4229 (103)
Pb	1623 ± 17	4460 (63)	843.6 ± 22	1288 (104)
Cr	240.9 ± 2.3	355 (37)	606.9 ± 32	375 (74)