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Speciation transformation of arsenic during municipal solid waste incineration

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Abstract

The release of arsenic (As) during municipal solid waste (MSW) incineration results in a new sources of anthropogenic arsenic contamination. Arsenic toxicity depends not only on the quantity but also on its speciation. At high temperatures, arsenic is predominantly present as vapors (As_2O_3(g)) and its speciation transformation is determined by the interactions between As_2O_3(g) and inorganic compounds. In this study, synchrotron X-ray absorption near-edge structure (XANES) was used to investigate the speciation transformation of arsenic during MSW combustion and flue gas cooling process. However, arsenates in various forms are hardly distinguished by using XANES alone. Considering that various arsenates are of different thermal stability, the thermal stability of arsenic in MSW incineration fly ash was examined to provide detailed information regarding arsenic speciation in the ash samples. To further understand the relationships between arsenic and inorganic compounds, the sequential extraction procedures of arsenic in the ash were conducted. The results show that the oxidation of As_2O_3(g) during MSW combustion is incomplete and is continuously performed in flue gas cooling process. The physical adsorption of As_2O_3(g) is favored at low temperature by ash particles, especially by the injection of CaO in the flue gas. Various kinds of arsenates are formed due to the interactions between As_2O_3(g) and Ca, Fe and/or Al compounds. Some of the arsenates are thermally unstable and are decomposed when the fly ash was heated at 1323 K. Part of arsenic is stabilized in the ash matrix including some un-oxidized As(III) which remained stable even when the ash was heated at 1323 K.

Keywords: MSW incineration; Arsenic; Speciation transformation; Thermal stability

1. Introduction

Recently, incineration has been widely used for the disposal of municipal solid waste (MSW) in China. In 2011, more than 25,000,000 tons of MSW is incinerated [1]. The release of arsenic during MSW incineration brings about a new sources of anthropogenic arsenic contamination [2]. The toxicity of arsenic depends not only on the quantity but also on its speciation. Arsenic in the form of arsenite (As(III)) is much more toxic than in the form of arsenate (As(V)) [3].

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Arsenic is predominantly present as vapors (As_2O_3(g)) in MSW incinerator when temperature exceeds 900 K [4,5]. The speciation transformation of arsenic during MSW incineration is mainly determined by the interactions between arsenic vapors and inorganic compounds. Calcium in MSW is of high content [6] which is effective for As_2O_3(g) capture at high temperatures by forming arsenates [7,8]. The effects for the capture of arsenic by calcium compounds differ for various forms of calcium. CaO is more effective than di-calcium silicate ($2CaO{\cdot}SiO_2$) and mono-calcium silicate ($CaO{\cdot}SiO_2$) [9]. However, acid gases in the flue gas like SO_2 compete with arsenic vapors to react with calcium compounds, suppressing arsenic capture [10]. Except for calcium compounds, other inorganic compounds in MSW such as iron oxides might also facilitate As_2O_3(g) capture by forming $FeAsO_4$ [10,11].

In China, both fluidized bed incinerators and grate incinerators are currently widely used for MSW incineration. Unlike the application of grate incinerator, coal is always added as a combustion improver for the application of fluidized bed incinerator [12]. Due to the different characteristics of coal and MSW, the contents of Ca, Fe, Si, S and Cl in the ash particles from these two types of incinerators are quite different [13]. The concentration of SO_2 and HCl in the flue gas in various incinerators are probably different due to the various combustion conditions [14,15]. As a result, the reactions between CaO and these acid gases differ in the two kinds of incinerators and calcium forms in the ash particles might be also different. Therefore, it is of great importance to understand the speciation transformation of arsenic during MSW incineration in various kinds of incinerators.

For the speciation determining of trace elements in ash residues, X-ray absorption spectroscopy is considered as a nondestructive method [16]. It has been used to study arsenic speciation in both coal fly ash and flue gas desulphurization residues [17,18]. However, arsenic spectra detected by synchrotron-based X-ray absorption near-edge structure (XANES) are similar for various forms of arsenates ($Ca_3(AsO_4)_2$, $FeAsO_4$ and $AlAsO_4$) [17]. It is difficult to further distinguish various kinds of arsenates by using XANES alone. Some researchers have found that various arsenates such as $Ca_3(AsO_4)_2$ and $FeAsO_4$ are of different thermal stability [11,19]. Coupled with the speciation investigation by XANES, the investigations of the arsenic thermal stability in MSW incineration fly ashes could provide more detailed information of arsenates in the ash samples. Besides, arsenic bound with various inorganic compounds like calcite and Fe/Al-oxides are usually distinguished through the sequential extraction procedures (SEP) [20,21]. The relationships between As and inorganic compounds might be well understood through SEP investigation.

The present study aims to illuminating the mechanism of arsenic speciation transformation during MSW incineration in both grate incinerator and fluidized bed incinerator. To assess the interactions between arsenic vapors and ash particles of various characteristics, the arsenic speciation in the ash samples from different incinerators were determined using XANES. Arsenic speciation in the fly ashes sampled from the same plants at different sites (namely, cyclone, superheater and fabric filters) downstream the flue gas were also investigated to observe the fate of arsenic during the flue gas cooling process. The speciation of arsenic in the ash samples was further observed by detecting the thermal stability of arsenic and through the investigation of the leaching behavior of arsenic during the sequential extraction procedures.

2. Experimental procedures

In this study, MSW incineration fly ash was sampled from fabric filters in plants located in various areas. Detailed information regarding each of the incinerators is shown in Table SI-1 (in Supporting information, SI). Fly ash labeled FBFA was sampled from fluidized bed incinerators and ash labeled GFA was sampled from grate incinerators. Cyclone ash (labeled CA, operating temperature about 1123 K) and superheater ash (labeled SA, operating temperature about 873 K) were sampled from the same incinerator as FBFA1. All the ash samples were dried to constant weight at 328 K for subsequent analysis and experiments.

The investigation of the thermal stability of arsenic in fly as was conducted by heating the ash samples in a horizontal furnace at 1323 K in air and N_2, respectively. The flow rate (1 L/min) of carrier gas was controlled using a mass flow controller and the thermal treatment of each ash sample was maintained for 2 h. Major components analyses of the ash samples were performed by X-ray fluorescence spectrometry (XRF). The free CaO (f-CaO) content in the ash samples was determined using the glycol method [22]. X-ray powder diffraction (XRD) was used to provide detailed information regarding the mineralogical characteristics of raw and thermal treated ash samples. The concentration of arsenic in the ash samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) after digestion by using HNO_3–HF–$HClO_4$ method [23]. The detection of arsenic concentration in all the samples was repeated more than three times to ensure the validity and reproducibility of the results.