



Speciation transformation of arsenic during municipal sewage sludge incineration with cotton stalk as additive



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HIGHLIGHTS

- Speciation transformation of As during co-firing of MSS and CS was studied.
- As(III) was gradually oxidized to As(V) as relative amount of CS increased.
- Ca, Al, and Fe compounds in CS provided chemical adsorption sites for arsenic.
- Oxidation of arsenic was continuously conducted during flue gas cooling process.

ARTICLE INFO

Article history:

Received 7 February 2017

Received in revised form 15 April 2017

Accepted 18 April 2017

Available online 24 April 2017

Keywords:

Municipal sewage sludge

Cotton stalk

Co-firing

Arsenic

Chemical oxidation

ABSTRACT

The fly ash from municipal sewage sludge (MSS) incineration contains abundant phosphorus and can be used as phosphate fertilizer. However, fly ash also contains arsenic that is extremely poisonous to the environment. The toxicity of arsenic significantly depends on its speciation: As(III) is much more toxic than As(V). Addition of cotton stalk (CS) was proposed to promote the speciation transformation of arsenic to the less harmful As(V) during MSS incineration. In this work, the speciation transformation of arsenic during the co-firing of MSS and CS in a fluidized bed was studied, and the fate of arsenic during flue gas cooling process was also investigated. The results indicate that the chemical oxidation of arsenic vapors ($\text{As}_2\text{O}_3(\text{g})$) is greatly stimulated by the co-firing of MSS and CS especially at 40–50% CS. Mineral compounds such as Ca, Fe, and Al compounds in CS can provide chemical adsorption sites for arsenic to facilitate the chemical oxidation of arsenic by forming various arsenates (As(V)) during MSS incineration. Additionally, the oxidation of arsenic is continuously conducted during flue gas cooling at 320–610 °C. The arsenic toxicity in the fly ash sampled downstream the flue gas was significantly reduced by addition of 40% CS into MSS during incineration.

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1. Introduction

Currently, over 24 million tons (wet weight) of municipal sewage sludge (MSS) are produced every year in China [1]. MSS incineration has been widely adopted to reduce the original mass and volume of MSS, and the resulting fly ash containing abundant phosphorus can be used as phosphate fertilizer [2,3]. However, arsenic emission during MSS incineration [4] can cause environmental toxicity [5,6]. The toxicity of arsenic greatly depends on its specific chemical forms and As(III) is much more toxic than As(V) [7]. Thus, it is essential to both control the overall release of

arsenic and reduce the released amount of the species with higher toxicity, As(III), during MSS incineration.

Arsenic is easily released mainly as vapors ($\text{As}_2\text{O}_3(\text{g})$) during MSS incineration [8,9]. The capture and speciation transformation of arsenic mainly depend on interactions between mineral compounds and arsenic vapors. The addition of mineral sorbents is a prospective approach to enhance the capture of trace metal vapors [10,11]. Zhao et al. [12] found that arsenic reacted with calcium-based sorbents to form calcium arsenates (As(V)) and was enriched in larger ash particles. Jadhav and Fan [13] reported that $\text{As}_2\text{O}_3(\text{g})$ could be captured by CaO through the formation of $\text{Ca}_2\text{As}_2\text{O}_7$ and $\text{Ca}_3\text{As}_2\text{O}_8$. The chemical oxidation of $\text{As}_2\text{O}_3(\text{g})$ can be performed over a wide temperature range, especially 303–900 °C [14]. The capacity of arsenic capture varies for different calcium compounds. Sterling and Helble [15] showed that arsenic capture by CaO was

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better than that by mono-calcium silicate ($\text{CaO}\cdot\text{SiO}_2$) and di-calcium silicate ($2\text{CaO}\cdot\text{SiO}_2$). However, fuel combustion releases acid gases like SO_2 that could also react with calcium compounds to compete with $\text{As}_2\text{O}_3(\text{g})$, inhibiting arsenic capture [16]. In addition to calcium compounds, Zhang et al. [17] maintained that ferric oxide (Fe_2O_3) could also promote the capture of $\text{As}_2\text{O}_3(\text{g})$ by forming iron arsenate (FeAsO_4). Arsenic vapors might also be absorbed by aluminum compounds [14].

Thus, during MSS incineration, the interactions between arsenic vapors and various inorganic compounds facilitate arsenic capture and the speciation transformation of As(III) into As(V). The proposal to co-fire biomass with MSS was proposed to realize the harmless transformation of some trace metals (Zn, As, and others), and our previous studies found the leaching toxicity of Zn and As in fly ash was reduced by the co-firing of MSS and biomass [18]. In addition, there are no alkali metal problems during the co-firing of MSS and biomass because the alkali metals can react with phosphorus in MSS to form high-melting-point compounds such as $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ [19,20]. The mineral matter in biomass may allow chemical adsorption and stimulate the chemical state transformation of arsenic during MSS incineration. However, the mechanism of arsenic speciation transformation during the co-firing of MSS and biomass has not been characterized.

The speciation transformation of arsenic during co-firing of MSS and CS was studied in this work. The experiments were conducted in a bubbling fluidized-bed combustor. The speciation (As(III) and As(V)) of arsenic in fly ash samples from co-firing of MSS and CS was investigated to clarify the behavior of arsenic speciation transformation. Arsenic speciation in the fly ash samples collected from different sampling sites in the flue during co-combustion of MSS and CS, was analyzed to determine the fate of arsenic during the cooling down of flue gas. To further explore the interactions between inorganic compounds and arsenic vapors, the speciation of arsenic in the fly ash samples was determined using sequential extraction procedures (SEP). Complexes of arsenic bound with different mineral compounds such as calcite and iron/aluminum oxides were observed using SEP [21–23].

2. Experiments

2.1. Materials

In this study, dewatered municipal sewage sludge (MSS) was collected from the Qinghe wastewater treatment plant in Beijing. Cotton stalk (CS) was selected as the straw sample and was obtained from Hebei province in northern China. MSS and CS samples were crushed into pellets smaller than 4 mm in diameter and dried to constant weight at $105\text{ }^\circ\text{C}$. The ultimate and proximate analysis of MSS and CS are shown in Table 1. The main inorganic elements in MSS and CS are listed in Table 2.

The crystalline phases in MSS and CS were identified by X-ray power diffraction (XRD, PANalytical, Netherlands). The XRD detector was equipped with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). The raw MSS and CS were ashed at $575\text{ }^\circ\text{C}$ to burn out the carbon in the samples before XRD testing [24]. Fig. 1 shows the crystalline phases in the MSS and CS ash. As shown in Table 2 and Fig. 1,

although the content of Ca in CS was lower than that in MSS, the forms of Ca in the MSS and CS samples were different. CaO is detected in CS but not in MSS. Previous studies showed that compared with other mineral compounds, CaO in CS is more effective for arsenic capture during MSS incineration [15,25]. In conclusion, the form of Ca in CS is more reactive than the form in MSS. Thereby, CS was chosen as a mineral additive during MSS incineration.

2.2. Apparatus and Analytical methods

Experiments were conducted in a 5 kW electrically heated bubbling fluidized-bed combustor. The schematic diagram of the experimental system is shown in Fig. 2. The bed pressure was measured using pressure transducers, and the bed temperature was monitored using a K-type thermocouple. Details of the system and the experimental process were described previously [20]. Different mass ratios of MSS to CS were tested, 10:0, 9:1, 8:2, 7:3, 6:4, and 5:5. The incineration temperature during co-firing of MSS and CS was maintained at $900 \pm 5\text{ }^\circ\text{C}$. Each test lasted for 4 h under stable operation conditions. The outlet temperature of the combustor was $700 \pm 5\text{ }^\circ\text{C}$. To more easily study the arsenic speciation transformation during the flue gas cooling process, the subsection water-cooling mode was adopted in the tail flue of the test bed, as shown in Fig. 2. Three fly ash sampling sites (sampling pipe 1 and 2, and ash bucket in the cyclone) were placed along the flue as indicated in Fig. 2, and the corresponding fly ash samples were FA1, FA2, and FA3, respectively. The temperature at the three sampling sites was measured by thermocouples during the experiments, and the measured temperature for FA1, FA2, and FA3 were $610 \pm 5\text{ }^\circ\text{C}$, $460 \pm 5\text{ }^\circ\text{C}$, and $320 \pm 5\text{ }^\circ\text{C}$, respectively.

The main inorganic elements in the raw materials were identified by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Thermo Fisher, IRIS Intrepid II XSP). The main chemical composition of the fly ash samples were determined by X-ray Fluorescence Spectrometer (XRF). The glycol method [26] was used to measure the amount of free CaO (f-CaO) in the fly ash samples. The physical properties of the fly ash samples were determined using a N_2 absorption apparatus (Demo 2020 V4.02), including pore volume and the BET specific surface area. The total concentrations of arsenic in the fly ash samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series). The concentrations of arsenate As(V) and arsenite (As(III)) were determined by ICP-MS coupled with ion chromatography (IC, Thermo ICS 2000). As(V) and As(III) were separated using an anion exchange column (Hamilton PRP-X100). The concentration of the separated As(V) and As(III) were measured separately by ICP-MS. All the tests were repeated at least three times to ensure the validity of the results.

To better understand the chemical state transformation of arsenic during co-firing of MSS and CS, the speciation of arsenic in the fly ash samples was analyzed according to the six-step sequential extraction procedure. The arsenic was classified as non-specifically adsorbed As, specifically adsorbed As, As bound with calcite, amorphous and poorly-crystalline As bound with Fe/Al oxides, well-crystallized As bound with Fe/Al oxides, and residual As [14,21,22].

Table 1
Proximate and ultimate analysis of MSS and CS (wt.%, as dry basis).

Fuel	Proximate Analysis			Ultimate Analysis					LHV (MJ/kg)
	Ash	Fixed carbon	Volatile	C	H	O	N	S	
MSS	33.39	9.69	56.92	34.85	4.92	19.92	5.99	0.93	13.67
CS	11.79	20.02	68.19	43.22	5.13	38.79	0.92	0.15	16.02

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