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Influence of operating parameters on arsenic transformation during municipal sewage sludge incineration with cotton stalk

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HIGHLIGHTS

- Capture of As was promoted with temperature increasing from 800 °C to 900 °C.
- Oxidation of $As_2O_3(g)$ was favored by forming various arsenates (As^{5+}) at 950 °C.
- As compounds in MSS like As_2S_3 reacted with O_2 to form $As_2O_3(g)$ at low O_2 content.
- Oxidation of As^{3+} to As^{5+} was stimulated at high O_2 content.

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ABSTRACT

Addition of cotton stalk (CS) has been proved to promote dramatically the transformation of toxic As^{3+} to less toxic As^{5+} in the fly ash during municipal sewage sludge (MSS) incineration. However, the fate of arsenic during co-firing of MSS and CS in different operating parameters was still unclear. In the present study, the effects of incineration temperatures and O_2 content in the flue gas on speciation transformation of arsenic during MSS and 70% MSS/30% CS incineration were investigated in a bubbling fluidized bed. The results show that less arsenic is distributed in bottom ash whereas more arsenic is migrated to the fly ash and flue gas, with the temperature increasing from 800 °C to 950 °C. The arsenic capture in fly ash is facilitated predominantly by the condensation and/or physical adsorption of $As_2O_3(g)$ at the temperatures from 800 °C to 900 °C. The chemical oxidation of $As_2O_3(g)$ is favored by forming various arsenates (As^{5+}) at 950 °C. At low O_2 content from 1% to 5%, some arsenic compounds in MSS such as As_2S_3 can react with O_2 to produce $As_2O_3(g)$, and then more $As_2O_3(g)$ is captured in the fly ash by the inherent mineral compounds like CaO through the condensation and/or physical adsorption. Further increasing O_2 content especially to 9% stimulates significantly the oxidation of As^{3+} to As^{5+} in the fly ash, which is mainly attributed to the chemical reactions between $As_2O_3(g)$, various mineral compounds and sufficient O_2.

1. Introduction

Municipal sewage sludge (MSS) incineration technology has been widely used for its entire disposal, heat energy recovery and resource recycle, and the ash is a source of phosphorus resource (Li et al., 2015, 2017; Nowak et al., 2012). However, MSS incineration has great environmental implications as the large quantities of MSS incinerated release undesirable amounts of harmful elements, even those trace elements such as arsenic. Toxic arsenic emission has aroused widespread concern of environmentalists. Other than the arsenic concentration in MSS and incineration ash, its forms of occurrence are equally significant because they greatly impact the release rate of arsenic into the atmosphere and the arsenic-related risks to human health (Low and Zhang, 2013; Zielinski et al., 2007). Arsenite (As^{3+}) is much more poisonous than arsenate (As^{5+}) (Tresintsi et al., 2014).

Arsenic is easily volatilized during MSS combustion, and enriched in the fly ash remarkably in As^{3+} form through the condensation and/or physical adsorption of vapors ($As_2O_3(g)$) (Chesworth et al., 1994; Contreras et al., 2009). Mineral additives are widely used to promote the capture and oxidation of arsenic

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vapors by forming various arsenates (As^{5+}), dramatically reducing the toxicity of arsenic in incineration ash (Low and Zhang, 2013; Zhang et al., 2015). Calcium and iron were found to play important roles in suppressing arsenic releasing from fuels in the process of thermal treatments (Guo et al., 2004; Wang and Tomita, 2003). The reaction mechanisms between Fe/Ca compounds and arsenic have been widely studied. It was reported that CaO could react with As_2O_3(g) and O_2(g) to form $Ca_3As_2O_8$ and $Ca_2As_2O_7$ (Jadhav and Fan, 2001). Shen et al. (2015) showed that arsenic compounds could react with CaO to produce $Ca(AsO_2)_2$ above 1000 °C by thermodynamic calculation. Zhao et al. (2008) demonstrated that Ca-based sorbent stimulated arsenic capture by generating calcium arsenates (As^{5+}). Zhang et al. (2015) substantiated that As_2O_3(g) could be oxidized by Fe_2O_3 and converted into iron arsenate ($FeAsO_4$). Arsenic might be captured by Al-containing compounds (Hu et al., 2015). In addition, all kinds of factors, such as retention time and temperature, were reported to affect the capacity of CaO and $CaSO_4$ for arsenic capture (Chen et al., 2015). Li et al. (2007) believed that arsenic capture was facilitated with temperature increasing from 600 °C to 1000 °C. Low and Zhang (2013) claimed that increasing the oxygen partial pressure, during oxy-fuel combustion with over 27% O_2 in O_2/CO_2 mixtures, stimulated the chemical oxidation of As^{3+} to As^{5+}.

Based on the results of former researchers, the addition of biomass into MSS during incineration was proposed to realize the speciation transformation of arsenic. Our previous studies indicated that co-firing of MSS and cotton stalk (CS), rich in Ca, Fe, Al, and Si compounds, could effectively promote speciation conversion of arsenic from As^{3+} to As^{5+} (Zhao et al., 2017b) and stabilization of Zn species in the fly ash (Zhao et al., 2017a), significantly reducing the toxicity of fly ash. This is beneficial for phosphorus reusing and recycling in the fly ash. Moreover, there were not agglomeration problems of alkali metals during co-firing of MSS and biomass (Li et al., 2013; Ren and Li, 2015).

However, the fate of arsenic during co-firing of MSS and CS (biomass selected) in different operating parameters, such as incineration temperature and excess air coefficient, is still unclear. Thereby, this work focuses on the speciation transformation of arsenic under different operating conditions during MSS incineration with and without CS.

2. Experimental procedures

2.1. Materials

Municipal sewage sludge (MSS) and cotton stalk (CS) were obtained from Beijing and Hebei Province, China, respectively. MSS and CS samples were broken into particles with a size of less than 4 mm and dried for 8 h at 105 °C prior to experiments. The properties of MSS and CS are listed in Table 1. The results show that the MSS has high content of ash whereas its lower heating value (LHV) is low. In contrast, the CS contains higher content of fixed carbon and volatile as well as the LHV, which can improve the combustion performance in the mixed fuels. The main elemental compositions of MSS and CS are presented in Table 2. The main mineral phases in the fuel samples were analyzed in our previous study, and it was found that the modes of occurrence of minerals (Ca, Fe, Al, etc.) were different (Zhao et al., 2017b). In particular, the free CaO (f-CaO) was remarkably found in the CS but not in MSS (Zhao et al., 2017b), which is more effective for arsenic capture than other mineral compounds (Chen et al., 2015; Sterling and Helble, 2003).

Table 1
Proximate and ultimate analysis of fuel samples (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

Table 2
Main elemental compositions of fuel samples (wt%, as dry basis).

Fuel	Al	Ca	Fe	K	Mg	P	Si	Na	Cl
MSS	1.76	1.77	1.58	1.06	0.95	1.06	5.27	0.33	0.03
CS	0.43	0.96	0.34	1.01	0.34	0.14	2.48	0.27	0.22

2.2. Apparatus and analytical methods

The combustion experiments were carried out in a 5 kW bubbling fluidized bed. The schematics of the experimental apparatus and its operation procedure were detailed elsewhere (Ren and Li, 2015; Zhao et al., 2017b). To study the influence of temperature on arsenic speciation transformation during MSS combustion with and without 30% (wt.%) CS in mixture, the combustion tests were conducted and lasted for 4 h at 800 ± 5 °C, 850 ± 5 °C, 900 ± 5 °C, and 950 ± 5 °C, respectively. To easily assess the effect of different excess air coefficients, the oxygen contents (vol%) in the exhaust flue gas were selected as study objects, 1%, 3%, 5%, 7%, and 9%, during co-firing of MSS with and without 30% CS. The O_2 concentration in flue gas was continuously measured via an on-line KM9106 gas analyzer. Bottom ash samples were collected from the pipe at the bottom of test bed, and fly ash samples were sampled from the ash bucket of cyclone separator.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was chosen to determine the main elemental compositions of fuel samples. X-ray fluorescence spectrometer (XRF) was used to analyze the main chemical compositions of the fly ash samples. The glycol method (Long et al., 2002) was employed to determine the content of f-CaO in the ash samples. Arsenic concentration in the ash samples was quantified using inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series). The instrumental parameters and analytical conditions were optimized to ensure sufficient sensitivity and precision. The power was 1200 W. The flow rate of cooling gas was 14.0 L min^{-1}. The flow rate of auxiliary gas was 0.8 L min^{-1}. The flow rate of carrier gas was 0.72 L min^{-1}. The sample uptake flow rate was 1 mL min^{-1}. The sampling depth was 2.8 mm. The sampling cone aperture was 1.0 mm, and the skimmer cone aperture was 0.7 mm. The contents of oxides and doubly charged ions were less than 2% and 3%, respectively. The concentrations of arsenate (As^{5+}) and arsenite (As^{3+}) in the samples were measured by ICP-MS coupled with ion chromatography (IC, Thermo ICS 2000). The separation of As^{5+} and As^{3+} was carried out using an anion exchange column (Hamilton PRP-X100). The concentration of the separated As^{5+} and As^{3+} were quantified by ICP-MS, respectively. In addition, the six-step sequential extraction procedures (SEP) for the ash samples were performed to investigate the modes of occurrence of arsenic (Hu et al., 2015; Pantuzzo and Ciminelli, 2010). The arsenic leached in the six steps represents six species, 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, respectively. All the tests were performed for at least three times to ensure the reproducibility of the results.