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 (As2O3(g)) and its speciation transformation is determined by the interactions between As2O3(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 As2O3(g) during MSW combustion is incomplete and is continuously performed in flue gas cooling process. The physical adsorption of As2O3(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 As2O3(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.

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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$_2$O$_3$(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$_2$O$_3$(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·SiO$_2$) and mono-calcium silicate (CaO·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$_2$O$_3$(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 ash 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.
The arsenic speciation in raw and thermally treated MSW incineration fly ash were measured by XANES at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. The data processing and spectra fitting were carried out by using ATHENA software. Sodium arsenite (NaAsO\textsubscript{2}) and arsenate (Na\textsubscript{2}HAsO\textsubscript{4}) were used as As(III) and As(V) standards which was described in details in our previous study [24].

The sequential extraction procedures of arsenic for each ash sample were carried out following 6 steps [20,21] as shown in Table SI-2. The leached arsenic from step 1 to step 6 represents arsenic in the phase of non-specifically adsorbed As, specifically adsorbed As, calcite-bound As, amorphous and poorly-crystalline Fe/Al-ox-bound As, well-crystallized Fe/Al-ox-bound As and residual As, respectively.

3. Results and discussion

3.1. Arsenic speciation in MSW incineration ash samples

The main compositions and arsenic concentration of the ash samples are shown in Table 1. Arsenic concentration in ashes from different sampling points in the same incinerator is in the following order, from highest to lowest: cyclone fly ash > fabric filter fly ash > superheater ash. The arsenic concentration in the fly ash from grate incinerator is much higher than in ash from fluidized bed incinerators. Few differences are found regarding the arsenic concentration in fly ash from various fluidized bed incinerators.

The arsenic speciation in the ash samples was determined by XANES and the spectra are shown in Fig. 1. The spectra of different ash samples are in a similar pattern with the same major energy peak as arsenate (Na\textsubscript{2}HAsO\textsubscript{4}) spectrum, indicating that most of arsenic is present in the form of As(V) in all samples. However, variations in the peak width and relative intensity suggest some differences. Specifically, the As(III)/As(V) ratios were different in various ash samples.

To address As(III)/As(V) ratios in these fly ashes, statistical analyses of arsenic speciation were carried out and the results are summarized in Table 2. The fraction of As(V) is higher in superheater ash and fabric filter fly ash, which were both sampled downstream the flue gas, than in cyclone ash. Few differences are found for arsenic speciation in various fluidized bed incinerators. However, more arsenic is found in the form of As(III) in fly ash from grate incinerators than in fly ash from fluidized bed incinerators.

As stated previously, As\textsubscript{2}O\textsubscript{3}(g) is the dominant arsenic compound in flue gas at high temperatures. The considerable amount of As(III) in cyclone ash is mainly attributed to the rapid condensation of As\textsubscript{2}O\textsubscript{3}(g) on the surfaces of ash particles [25] and/or the stabilization of arsenic in the form of As(III) into ash matrix, such as the glass phase [24,26]. The results also demonstrate that

![Fig. 1. Arsenic XANES spectra for MSW incineration ash samples and the standard materials (arsenite (NaAs\textsubscript{2}O\textsubscript{2}) and arsenate (Na\textsubscript{2}HAsO\textsubscript{4})).](image)

Table 1

<table>
<thead>
<tr>
<th>Compositions (%)</th>
<th>CA</th>
<th>SA</th>
<th>FBFA1</th>
<th>FBFA2</th>
<th>FBFA3</th>
<th>GFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>33.42</td>
<td>31.27</td>
<td>31.70</td>
<td>30.27</td>
<td>28.90</td>
<td>4.12</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>11.83</td>
<td>12.46</td>
<td>13.34</td>
<td>12.90</td>
<td>13.72</td>
<td>0.85</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>7.98</td>
<td>6.19</td>
<td>5.87</td>
<td>5.72</td>
<td>10.46</td>
<td>1.04</td>
</tr>
<tr>
<td>CaO</td>
<td>22.54</td>
<td>19.6</td>
<td>20.46</td>
<td>18.84</td>
<td>15.45</td>
<td>34.72</td>
</tr>
<tr>
<td>MgO</td>
<td>2.35</td>
<td>2.98</td>
<td>3.02</td>
<td>3.60</td>
<td>2.79</td>
<td>1.33</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>2.10</td>
<td>3.64</td>
<td>2.56</td>
<td>2.15</td>
<td>1.93</td>
<td>4.46</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>2.24</td>
<td>4.70</td>
<td>2.72</td>
<td>2.17</td>
<td>1.95</td>
<td>8.11</td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
<td>8.03</td>
<td>8.64</td>
<td>3.98</td>
<td>3.75</td>
<td>7.34</td>
<td>5.45</td>
</tr>
<tr>
<td>Cl</td>
<td>0.52</td>
<td>2.46</td>
<td>3.35</td>
<td>3.05</td>
<td>1.95</td>
<td>16.72</td>
</tr>
<tr>
<td>f-CaO</td>
<td>0.54</td>
<td>0.17</td>
<td>1.39</td>
<td>1.00</td>
<td>0.85</td>
<td>9.58</td>
</tr>
<tr>
<td>LOI</td>
<td>3.21</td>
<td>3.13</td>
<td>8.15</td>
<td>13.22</td>
<td>10.62</td>
<td>21.27</td>
</tr>
<tr>
<td>As/mg kg\textsuperscript{-1}</td>
<td>54.34</td>
<td>48.55</td>
<td>51.33</td>
<td>43.14</td>
<td>48.48</td>
<td>78.66</td>
</tr>
</tbody>
</table>

Notes: CA: cyclone ash; SA: superheater ash; FBFA: fabric filter fly ash from fluidized bed incinerator; GFA: fabric filter fly ash from grate incinerator; f-CaO, free CaO.
the oxidation of $\text{As}_2\text{O}_3(g)$ is incomplete in transforming As(III) into As(V) during MSW combustion which is mainly due to the slow oxidation rate and short residence time. The interactions between arsenic vapors and inorganic compounds such as calcium compounds stimulated the formation of arsenates in the fly ash over a large temperature range, specifically 576–1173 K [7–9,27]. As a result, the fraction of As(V) in fly ashes sampled downstream the flue gas is higher than elsewhere. However, acid gases such as SO$_2$ in flue gas could also react with CaO which is confirmed by the large fraction of Ca in the form of calcium sulfate in the cyclone fly ash and superheater ash as shown in Fig. SI-1. And the relative amount of effective calcium compounds for $\text{As}_2\text{O}_3(g)$ oxidation such as f-CaO is low as shown in Table 1. In this way, the oxidation of $\text{As}_2\text{O}_3(g)$ is limited during flue gas cooling process and a considerable amount of arsenic is still present in the form of As(III) in the superheater ash and fabric filter fly ash.

Further downstream, the retention of arsenic into the fly ash is most likely due to the physical adsorption of $\text{As}_2\text{O}_3(g)$ in the flue gas at low temperatures [19]. Usually, CaO is used for the removal of hazardous emissions in MSW incineration flue gas in China which is confirmed by that the amount of f-CaO in FBFA1 is higher than in the cyclone ash and superheater ash. The addition of CaO enhances the physical adsorption of $\text{As}_2\text{O}_3(g)$. Meanwhile, the content of chlorides is also higher in fabric filter fly ash, demonstrating that most chlorides are captured during the CaO spraying process. Chlorides present in the flue gas compete with arsenic vapors to be adsorbed by fly ash particles resulting in the inhabitation of arsenic capture. In fly ash from fluidized bed incinerators, the f-CaO is low and the physical adsorption of $\text{As}_2\text{O}_3(g)$ is limited. For GFA rich in f-CaO, the physical adsorption of $\text{As}_2\text{O}_3(g)$ is remarkable and more arsenic is in the form of As(III). This shows that the high concentration of arsenic in GFA is mainly due to the enhancement of physical adsorption of $\text{As}_2\text{O}_3(g)$.

### 3.2. The investigation of thermal stability and SEP of arsenic in the MSW incineration fabric filter ash

Figure 2 shows the arsenic volatile fractions that emerged during thermal treatment of the ash from various MSW incineration fabric filters. About 10–32% of the arsenic present in fly ash is released at 1323 K. More arsenic is volatilized in FBFA than in GFA. Few differences in the arsenic volatile fractions are observed in different atmospheres for thermal treatment of FBFA. However, more arsenic is volatilized in N$_2$ than that in air for GFA.

The arsenic speciation in thermal treated fly ashes are also determined using XANES and arsenic spectra for raw and thermal treated ashes are compared in Fig. 3. Like raw fly ash, the energy positions of arsenic spectra for the major peak of the thermally treated ash samples were the same as arsenate spectrum, indicating that As(V) was also the main form of arsenic in thermally treated ashes. Table 3 shows the distribution of arsenic speciation in thermal treated ash samples. As(V) fractions in all ash samples increase after thermal treatment in air. When ashes are thermally treated in N$_2$, As(V) fractions in GFA are higher than in raw fly ash, but these from FBFA are lower. Nevertheless, the results shown in Table 3 provide the relative contents of As(III)/As(V) in thermally treated ash. The arsenic speciation transformation during thermal treatment is hardly determined by a comparison of the relative contents of As(III)/As(V) in raw and thermally treated fly ash. Therefore, the absolute contents of As(III) and As(V) were calculated as follows:

$$\text{Absolute content} = (100 - \text{Volatile fraction} \times \text{Species content(%)})$$

### Table 2 Distribution of As speciation in MSW incineration ash samples.

<table>
<thead>
<tr>
<th>Species (%)</th>
<th>CA</th>
<th>SA</th>
<th>FBFA1</th>
<th>FBFA2</th>
<th>FBFA3</th>
<th>GFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenite (As$^{3+}$)</td>
<td>45.9</td>
<td>34.7</td>
<td>23.9</td>
<td>32.3</td>
<td>25.4</td>
<td>47.6</td>
</tr>
<tr>
<td>Arsenate (As$^{5+}$)</td>
<td>54.1</td>
<td>65.3</td>
<td>76.1</td>
<td>67.7</td>
<td>74.6</td>
<td>52.4</td>
</tr>
</tbody>
</table>

**Fig. 2.** Arsenic volatile fractions in various MSW incineration fabric filter ashes during thermal treatment at 1323 K in air and N$_2$. 

The oxidation of $\text{As}_2\text{O}_3(g)$ is incomplete in transforming As(III) into As(V) during MSW combustion which is mainly due to the slow oxidation rate and short residence time. The interactions between arsenic vapors and inorganic compounds such as calcium compounds stimulated the formation of arsenates in the fly ash over a large temperature range, specifically 576–1173 K [7–9,27]. As a result, the fraction of As(V) in fly ashes sampled downstream the flue gas is higher than elsewhere. However, acid gases such as SO$_2$ in flue gas could also react with CaO which is confirmed by the large fraction of Ca in the form of calcium sulfate in the cyclone fly ash and superheater ash as shown in Fig. SI-1. And the relative amount of effective calcium compounds for $\text{As}_2\text{O}_3(g)$ oxidation such as f-CaO is low as shown in Table 1. In this way, the oxidation of $\text{As}_2\text{O}_3(g)$ is limited during flue gas cooling process and a considerable amount of arsenic is still present in the form of As(III) in the superheater ash and fabric filter fly ash.

Further downstream, the retention of arsenic into the fly ash is most likely due to the physical adsorption of $\text{As}_2\text{O}_3(g)$ in the flue gas at low temperatures [19]. Usually, CaO is used for the removal of hazardous emissions in MSW incineration flue gas in China which is confirmed by that the amount of f-CaO in FBFA1 is higher than in the cyclone ash and superheater ash. The addition of CaO enhances the physical adsorption of $\text{As}_2\text{O}_3(g)$. Meanwhile, the content of chlorides is also higher in fabric filter fly ash, demonstrating that most chlorides are captured during the CaO spraying process. Chlorides present in the flue gas compete with arsenic vapors to be adsorbed by fly ash particles resulting in the inhabitation of arsenic capture. In fly ash from fluidized bed incinerators, the f-CaO is low and the physical adsorption of $\text{As}_2\text{O}_3(g)$ is limited. For GFA rich in f-CaO, the physical adsorption of $\text{As}_2\text{O}_3(g)$ is remarkable and more arsenic is in the form of As(III). This shows that the high concentration of arsenic in GFA is mainly due to the enhancement of physical adsorption of $\text{As}_2\text{O}_3(g)$.
The absolute contents of As(III)/As(V) in raw and thermal treated fly ash are compared in Fig. 4. Both As(III) and As(V) contents decrease after thermal processing in air in FBFA. It could be concluded that the release of arsenic during thermal treatment is not only attributable to the desorption of physically adsorbed As$_2$O$_3$ but also to the decomposition of thermal unstable arsenates such as Ca$_2$As$_2$O$_7$ and FeAsO$_4$ which are decomposed at temperatures higher than 1273 K.

**Table 3**

<table>
<thead>
<tr>
<th>Species ( Species (%)</th>
<th>FBFA1 Air</th>
<th>FBFA1 Nitrogen</th>
<th>FBFA3 Air</th>
<th>FBFA3 Nitrogen</th>
<th>GFA Air</th>
<th>GFA Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenite (As$^{3+}$)</td>
<td>13.2</td>
<td>25.5</td>
<td>23.5</td>
<td>37.1</td>
<td>35.2</td>
<td>21.1</td>
</tr>
<tr>
<td>Arsenate (As$^{5+}$)</td>
<td>86.8</td>
<td>74.5</td>
<td>76.5</td>
<td>62.9</td>
<td>64.8</td>
<td>78.9</td>
</tr>
</tbody>
</table>

Fig. 4. Absolute contents of As(III)/As(V) in raw and thermally treated fly ashes (TFA) at 1323 K in air and N$_2$ (a) FBFA1 (2) FBFA3 (3) GFA.
Therefore, various kinds of arsenates are supposed to be formed during MSW incineration and the flue gas cooling process due to the interactions of As\(_2\)O\(_3\)\((g)\) between different inorganic compounds. Some arsenic in the form of As(III) is still present in the fly ash after thermal treatment. These arsenic compounds are probably immobilized in the ash matrix [26]. Arsenic compounds in the form of As(V) could also be immobilized in the ash matrix and remain stable during thermal processing.

Compared with the thermal treatment in air, it is found that there is a larger decrease in As(V) content during thermal treatment in N\(_2\). The f-CaO probably reacts with the decomposed/adsorbed As\(_2\)O\(_3\) by forming thermally stable calcium arsenates in air which is suppressed in oxygen-lean N\(_2\). As a result, a greater fraction of arsenic is found in the form of As(V) in the thermally treated ash in air and less arsenic is volatilized as shown in Fig. 2. However, the content of f-CaO is low and the contents of Si and Al compounds are high in FBFA. Most of the CaO is transformed into calcium aluminosilicates in the thermally treated ashes [13] and the oxidation of arsenic is partly inhibited. Meanwhile, the formation of aluminosilicates promoted the immobilization of As(III), which is obvious in thermally treated ash in N\(_2\).

For GFA, although the content of f-CaO is high, the content of As(III) decreased remarkably in thermal treated ash in air which is mainly due to the slow oxidation of As(III) at the presence of CaO. Interestingly, the content of As(V) increases in the thermally treated ash in N\(_2\) demonstrating the oxidation of As(III) is taken place in oxygen-lean atmosphere. It is supposed that oxygen contained in the fly ash supports the oxidation of As(III). This hypothesis is supported by Sterling and Helble’s study [9], which shows that oxygen in reactants promotes the arsenic oxidation and that CaO is capable of reacting with arsenic vapor species by forming calcium arsenates in both air and nitrogen. Comparing with the decreases of As(III) contents during thermal
4. Conclusions

The speciation transformation of arsenic during MSW incineration and flue gas cooling process were investigated by using several analytical methods, including XANES, thermal stability investigation and sequential extraction procedures. Arsenic is enriched into the MSWI fly ash through physical adsorption, chemical oxidation and the stabilization by ash matrix. At operating temperature for MSW incineration, a large fraction of arsenic volatilizes. The interactions between arsenic vapors and Ca, Fe and/or Al compounds contribute to the chemical oxidation of arsenic by forming various kinds of arsennes. The oxidation of arsenic is incomplete during the combustion process and is continuously taken place in the flue gas cooling process. The capture of arsenic through the physical adsorption is enhanced at low temperature especially under the influence of the injected CaO. Apart from the volatilized fraction, part of arsenic is stabilized in the ash matrix which remains stable even when the ash was heated at 1323 K.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.06.052.

References
