Trace elements in co-combustion of solid recovered fuel and coal

Wu, Hao; Glarborg, Peter; Jappe Frandsen, Flemming; Dam-Johansen, Kim; Jensen, Peter Arendt; Sander, Bo

Published in:
Fuel Processing Technology

Link to article, DOI:
10.1016/j.fuproc.2011.05.007

Publication date:
2013

Citation (APA):
Trace elements in co-combustion of solid recovered fuel and coal

Hao Wu a,⁎, Peter Glarborg a, Flemming Jappe Frandsen a, Kim Dam-Johansen a, Peter Arendt Jensen a, Bo Sander b

aDepartment of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark
bDONG Energy Power A/S, Kraftvej 53, 7000 Fredericia, Denmark

A R T I C L E   I N   P R E S S

Article history:
Received 7 January 2011
Received in revised form 27 April 2011
Accepted 10 May 2011
Available online xxxx

Abstract
Trace element partitioning in co-combustion of a bituminous coal and a solid recovered fuel (SRF) was studied in an entrained flow reactor. The experiments were carried out at conditions similar to pulverized coal combustion, with SRF shares of 7.9 wt.%, 14.8 wt.% and 25.0 wt.%. In addition, the effect of additives such as NaCl, PVC, ammonium sulphate, and kaolinite on trace element partitioning was investigated. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn, since these elements were significantly enriched in SRF as compared to coal. During the experiments, bottom ash was collected in a chamber, large fly ash particles were collected by a cyclone with a cut-off diameter of ~2.5 μm, and the remaining fly ash particles were gathered in a filter. It was found that when coal was co-fired with SRF, the As, Cd, Pb, Sb and Zn content in filter ash/cyclone ash increased almost linearly with their content in fuel ash. This linear tendency was affected when the fuels were mixed with additives. The volatility of trace elements during combustion was assessed by applying a relative enrichment (RE) factor, and TEM–EDS analysis was conducted to provide qualitative interpretations. The results indicated that As, Cd, Pb, Sb and Zn were highly volatile when co-firing coal and SRF, whereas the volatility of Cr was relatively low. Compared with coal combustion, co-firing of coal and SRF slightly enhanced the volatility of Cd, Pb, Zn, but reduced the volatility of Cr and Sb. The Cl-based additives increased the volatility of Cd, Pb and As, whereas addition of ammonium sulphate generally decreased the volatility of trace elements. Addition of kaolinite reduced the volatility of Pb, while the influence on other trace elements was insignificant. The results from the present work imply that trace element emission would be significantly increased when coal is co-fired with SRF, which may greatly enhance the toxicity of the dusts from coal-fired power plant. In order to minimize trace element emission in co-combustion, in addition to lowering the trace element content in SRF, utilizing SRF with low Cl content and coal with high S and aluminosilicates content would be desirable.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction
Trace element emission is one of the major environmental concerns for pulverized coal-fired power stations. During pulverized coal combustion, the trace elements in the fuel usually undergo complicated chemical and physical transformations, and a fraction is eventually emitted to the atmosphere as dust or vapor [1–7]. Due to the adverse health effect [1], it is desirable to control the emission of trace elements from coal-fired power stations.

Co-combustion of coal and secondary fuel such as biomass and waste is recognized as a promising approach to reduce the CO2 emission from pulverized coal-fired power stations [8]. The typical secondary fuels are biomass such as straw [9,10] and wood [11], and waste derived fuels such as sewage sludge [4] and refuse derived fuels [12–15]. When biomass is used as the secondary fuel in co-combustion, the emission of trace elements is usually not of great concern, since the trace element content in most biomass is much lower than that of coal. In contrast, waste derived fuels are often characterized by a significantly larger trace element concentration than coal [4,14]. Thus it is of importance to characterize the behavior of trace elements during co-combustion of coal and waste derived fuel.

The behavior of trace elements during pulverized fuel combustion is well-known to be influenced both by the fuel properties and combustion conditions. The trace elements present in the fuels can be categorized as organic association (elements that are organically bounded, ionically bounded, or water soluble) and mineral association (elements that are present as included or excluded minerals) [2]. Extensive studies on the association of trace elements in different coals have been performed [1,2,6,16,17]. Similar investigations were also carried out on waste derived fuels such as sewage sludge [5] and refuse-derived char [18]. These studies generally suggest that the organically associated trace elements are more easily to vaporize during combustion than those associated with minerals [1]. On the
other hand, the vaporization behavior of trace elements is also influenced by parameters such as combustion temperature, transport/mixing phenomena, oxidizing/reducing condition, and the presence of gaseous species such as HCl and SO₂ [3]. In most cases, the presence of gaseous chloride may shift the distribution of trace elements such as Pb and Cd towards more volatile chlorides, thus promoting the vaporization [1,3,19]. However, the presence of SO₂ may result in the formation of sulphates with relatively low vapor pressure [19].

After being vaporized from the fuel, the trace elements may undergo reactions both with the ash particles and the gaseous species in the flue gas [19,20]. The reactions between the vaporized trace elements and the ash particles constitute an important mechanism for the retention of trace elements in large fly ash particles that are easier to be captured by the air pollution control systems [1,2]. Typical examples are the reactions between trace elements such as Cd and Pb and aluminosilicates such as kaolinite [20]. Such reactions occur primarily on the particle external surface and may result in trace element concentration in the ash particle being proportional to 1/dₚ, (particle diameter) [1,21-23]. On the other hand, the vaporized trace elements may also react with other gaseous species in the flue gas, such as HCl and SO₂. These reactions can alter the condensation behavior of the trace elements. In addition, they may influence the reactions between the vaporized trace elements and ash particles, since trace element in different gaseous forms (such as chlorides or hydroxides) may have different reaction rates with the ash particles [1].

When the flue gas temperature becomes lower than the dew point of a trace element species, condensation may occur on the surface of the existing ash particles. For ash particles in the continuum regime (supermicron particles with Kn<~1) condensation may lead to the trace element concentration in the ash particles being proportional to 1/dₚ², while for particles in the free molecular regime (ultrafine particles with Kn>>1) the concentration of the condensed trace element may be proportional to 1/dₚ [21-23]. One should be aware that the correlations mentioned earlier are based on several assumptions which may deviate from practical situations, such as perfect spherical and nonporous particles [23]. Therefore care must be taken in applying these theoretical correlations in practice.

All of the mechanisms mentioned earlier can influence the partitioning of trace elements in combustion. For a practical combustion system, the partitioning of trace elements involves complex processes such as vaporization, reaction, nucleation, condensation and coagulation. These processes become more complicated when a secondary fuel is introduced to the system, since it may have different fuel properties and combustion behavior as compared with the primary fuel. In order to evaluate the behavior of trace elements during co-combustion in a pulverized coal-fired plant, performing controlled experiments at combustion conditions similar to a practical plant is an advantageous approach.

The objective of the present work was to study the partitioning of trace elements in co-combustion of coal and solid recovered fuel (SRF) at conditions similar to a pulverized coal-fired plant. This was achieved by performing experiments in an entrained flow reactor, and by investigating the trace element partitioning in different ash fractions (bottom ash, cyclone ash and filter ash). It should be noted that the conditions in the entrained flow reactor are not fully representative of a pulverized coal-fired plant, with respect to particle residence time, temperature profile and fluid flow. Therefore the results from the present work may not fully represent the practical situation. The trace elements studied were As, Cd, Cr, Pb, Sb and Zn. These elements were emphasized since their content in the SRF was significantly (~5–150 times) larger than that of coal. The experiments were carried out at coal combustion with different SRF share conditions (7.9 wt.%, 14.8 wt.% and 25.0 wt.%, wet basis). In addition, the effect of additives such as NaCl, PVC, ammonium sulphate, and kaolinite on the behavior of trace elements was investigated. These additives were selected since they may have notable effect on the partitioning of trace elements [19,20]. Therefore the results from the present work could provide suggestions for trace element emission control in co-combustion of coal and SRF, through a systematic assessment of the behavior of trace elements at different fuel conditions.

2. Experimental

2.1. Fuels and additives

The fuels used in the experiments were a Columbian bituminous coal and a SRF mainly comprised of waste paper, plastics and wood. The selected additives were PVC, NaCl, (NH₄)₂SO₄ (denoted as AmSulf) and kaolinite, which are all pure compounds purchased from chemical companies. The properties of the fuels are listed in Table 1. It can be seen that the SRF has relatively larger volatile, C1 and Ca content than the coal, while it is lower in S, Si, Al and K. The trace element content in the two fuels is significantly different. The content of As, Cd and Cr in the SRF is 5–10 times larger compared to the coal. For Pb, Sb and Zn, the content in the SRF is 30–150 times larger than that of coal.

The SRF used in the present work has been pulverized by an Alpine® pin mill. Although SRF is normally regarded as a heterogeneous fuel, the grinding process has significantly improved the homogeneity of the SRF. For confirmation, the Si and Al content in the SRF have been analyzed 3 times and the average deviations were found to be 9% and 13%, respectively. This indicates that the SRF is quite homogeneous. In addition, the homogeneity of the SRF has been further evaluated by performing repeating co-combustion experiments, showing a good reproducibility of the NO and SO₂ emission during co-combustion of coal and SRF (average deviation <2%).

The particle size distribution of the fuels and additives was analyzed by a laser diffraction method (Malvern Mastersizer 2000 particle size analyzer). The dₐ₀ (meaning that 50 vol.% of the particles are below this size) of the SRF is approximately 164 μm, whereas the dₐ₀ of the coal is about 19 μm. The dₐ₀ of PVC, NaCl, AmSulf, and kaolinite is about 104 μm, 259 μm, 222 μm, and 8 μm, respectively. It should be noted that the SRF particles used in the present work tend to form clusters, whereas the other fuel/additive particles do not have such behavior.

2.2. Setup

The co-combustion experiments are carried out in an entrained flow reactor shown schematically in Fig. 1. The setup consists of a gas supplying system, a fuel feeding system, a gas preheater, a vertical reactor electrically heated by 7 heating elements, a bottom chamber, a particle and gas extraction system, and an ash deposition system simulating deposit formation on the superheater tubes of a boiler. The

<table>
<thead>
<tr>
<th>Properties</th>
<th>Coal</th>
<th>SRF</th>
<th>Properties</th>
<th>Coal</th>
<th>SRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV (MJ/kg wet)</td>
<td>26.53</td>
<td>20.86</td>
<td>Mg (wt.% dry)</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Moisture (wt.% wet)</td>
<td>5.25</td>
<td>5.20</td>
<td>P (wt.% dry)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Volatiles (wt.% wet)</td>
<td>34.11</td>
<td>72.05</td>
<td>Ca (wt.% dry)</td>
<td>0.18</td>
<td>0.67</td>
</tr>
<tr>
<td>Ash (wt.% wet)</td>
<td>10.42</td>
<td>5.69</td>
<td>Na (wt.% dry)</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>C (wt.% dry)</td>
<td>71.00</td>
<td>58.00</td>
<td>K (wt.% dry)</td>
<td>0.21</td>
<td>0.09</td>
</tr>
<tr>
<td>H (wt.% dry)</td>
<td>4.90</td>
<td>6.60</td>
<td>As (ppm dry)</td>
<td>3.71</td>
<td>18.9</td>
</tr>
<tr>
<td>N (wt.% dry)</td>
<td>1.50</td>
<td>1.00</td>
<td>Cd (ppm dry)</td>
<td>0.20</td>
<td>1.07</td>
</tr>
<tr>
<td>S (wt.% dry)</td>
<td>0.70</td>
<td>0.42</td>
<td>Cr (ppm dry)</td>
<td>15.2</td>
<td>178.0</td>
</tr>
<tr>
<td>Cl (wt.% dry)</td>
<td>0.03</td>
<td>0.28</td>
<td>Pb (ppm dry)</td>
<td>7.35</td>
<td>206.1</td>
</tr>
<tr>
<td>Si (wt.% dry)</td>
<td>3.06</td>
<td>1.08</td>
<td>Sb (ppm dry)</td>
<td>1.0</td>
<td>51.5</td>
</tr>
<tr>
<td>Al (wt.% dry)</td>
<td>1.21</td>
<td>0.21</td>
<td>Zn (ppm dry)</td>
<td>25.2</td>
<td>3500</td>
</tr>
</tbody>
</table>

Please cite this article as: H. Wu, et al., Trace elements in co-combustion of solid recovered fuel and coal. Fuel Processing Technol. (2011), doi:10.1016/j.fuproc.2011.05.007
vertical reactor, which contains the combustion zone, is made of silicon carbide (SiC), and has a length of 2 m and a diameter of 0.08 m. A more detailed description of the setup can be found elsewhere [9]. During the experiments, the premixed fuels are injected into the reactor together with the primary air. The fuel particles are mixed with the preheated secondary air at the inlet of the vertical reactor, and subsequently combusted in the reactor. The flow rates of the primary air and secondary air is maintained at 13 Nl/min and 82 Nl/min, respectively. The temperature of the heating elements in the preheater is 900 °C. In order to simulate a high temperature environment comparable to a pulverized coal-fired plant, the wall temperature of the vertical reactor is set to 1000–1300 °C for all of the experiments. The mean gas velocity in the reactor is approximately 1.7 m/s, assuming an average gas temperature of 1200 °C. When the fuels are combusted in the reactor, the bottom ash is collected in a chamber. The flue gas together with the fly ash particles are separated into two fractions. As shown in Fig. 1, a part of the flue gas with temperature about 600 °C is drawn to an extraction system through a water-cooled probe. The large fly ash particles are collected by a cyclone with a cut-off diameter of 3.5 μm, and the fly ash particles passing through the cyclone are gathered in an aerosol filter equipped with a polycarbonate membrane having a pore size of 0.1 μm. The remaining flue gas from the combustion is directed towards a deposition probe which simulates the superheater tube in a boiler. Prior to the start of an experiment, combustion is performed for 40 min to achieve a more stable condition in the reactor. The duration of an experiment is 1.5 h, after which the deposit on the probe, the ash from extraction tubes, cyclone, aerosol filter, and bottom chamber are collected, weighted and preserved for analysis. In order to minimize the contamination from the previous experiment, the reactor is heated to 1400 °C for 20 h after every experiment, to perform high temperature cleaning. A more detailed description of the experimental procedures is given elsewhere [12].

2.3. Experimental matrix

As shown in Table 2, the experiments carried out in the present work include coal combustion, co-combustion of coal and SRF, and co-combustion of coal with a mixture of SRF and additive. During co-firing coal and SRF, the mass share of SRF was 7.9 wt.% (wet basis), 14.8 wt.% and 25.0 wt.%, respectively. For the experiments with additives, the mass share of coal was maintained at 85.2 wt.%, meaning that the mass share of the mixture of SRF and additive was 14.8 wt.%. With fixed mass share of coal, the addition of additives simulated a significant variation of the SRF properties. The addition of NaCl (1 wt.% and 2 wt.%) corresponded to a SRF with a high alkali chloride content, while the addition of PVC (2 wt.% and 4 wt.%) enhanced the chlorine content of the SRF. The addition of ammonium sulphate (AmSulf) or kaolinite allowed us to study trace element behavior under conditions with high sulphur and aluminosilicates concentration in flue gas. To assure all of the experiments are carried out at similar combustion conditions, the excess air ratio for different experiments was maintained around 1.43, as shown in Table 2.

2.4. Fuel and ash analysis

The elemental composition of the fuel and ash samples from the experiments was analyzed at Enstedværket Laboratory, DONG Energy A/S. The content of the major and trace elements in the fuel, bottom ash, cyclone ash, and filter ash was determined by ICP-OES (inductively coupled plasma optical emission spectrometry) or IC (ion chromatography). The IC was mainly applied to analyze the Cl and S content, while the remaining major and trace elements were analyzed by ICP-OES. Besides the bulk chemical analysis, the typical morphology and composition of the filter ash from selected experiments were characterized by using TEM–EDS (transmission electron microscopy and dispersive X-rays spectroscopy).

3. Results and discussion

3.1. Mass balance

The mass balance for different experiments has been calculated based on the fuel and ash composition, the fuel feeding rate, the amount of the collected ash and the corresponding flue gas flow rate. Fig. 2 shows the mass balance of ash, Si, and trace elements. It is seen that the ash balance for most of the experiments is between 80% and 90%. The ash balance is all below 100%, primarily due to the deposition of ash in the reactor tube which can be observed after experiments. In addition, although the ash is collected carefully during the experiments, some fly ash may remain in the sampling system after collection, which also influences the ash balance. The mass balance for the major inorganic elements is mostly between 70% and 90%, which is similar to the ash balance. As an example, the mass balance of the element Si and Al is shown in Fig. 2.

In comparison with the major inorganic elements, the mass balance of the trace elements is generally less satisfactory. This is presumably related to the analysis uncertainties of the trace element concentrations in the SRF. It is well-known that the content of trace elements in different waste fractions can deviate significantly [24]. Although the SRF used in the experiments has been homogenized through the production and grinding processes, the SRF sample selected for analyzing trace element content may not be fully representative, primarily due to the small amount (~0.4 g) of sample selected for analysis. This may be reflected by the increased mass balance of Cd with increasing share of SRF, which suggests that the Cd content in the SRF might be underestimated. For Sb and Zn, the

Table 2

<table>
<thead>
<tr>
<th>Experimental number</th>
<th>Fuel composition wt.%</th>
<th>Excess air ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 – – – – – –</td>
<td>1.44</td>
</tr>
<tr>
<td>2</td>
<td>92.1 7.9 – – – – –</td>
<td>1.43</td>
</tr>
<tr>
<td>3</td>
<td>85.2 14.8 – – – – –</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>75 25.0 – – – – – –</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>85.2 13.8 1.0 – – –</td>
<td>1.42</td>
</tr>
<tr>
<td>6</td>
<td>85.2 12.8 2.0 – – –</td>
<td>1.42</td>
</tr>
<tr>
<td>7</td>
<td>85.2 12.8 – 2.0 – –</td>
<td>1.43</td>
</tr>
<tr>
<td>8</td>
<td>85.2 10.8 – 4.0 – –</td>
<td>1.43</td>
</tr>
<tr>
<td>9</td>
<td>85.2 10.8 – – 4.0 –</td>
<td>1.42</td>
</tr>
<tr>
<td>10</td>
<td>85.2 10.8 – – – 4.0</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Please cite this article as: H. Wu, et al., Trace elements in co-combustion of solid recovered fuel and coal, Fuel Process. Technol. (2011), doi:10.1016/j.fuproc.2011.05.007
decreasing tendency with increasing share of SRF indicates that the content of Sb and Zn in SRF may be over-estimated. Besides the analysis uncertainties, the collection efficiency of different ash fractions may also influence the mass balance, since the distribution of trace elements in different ash fractions is more uneven compared to the major inorganic elements. Considering the uncertainties, it is suggested to focus on the tendencies shown in the present work, rather than the accurate numbers.

3.2. Trace element content in the cyclone ashes and filter ashes

In order to assess the influence of co-combustion on the trace element content in fly ash, the trace element content in the filter ash and the cyclone ash collected from the experiments are plotted versus the content in the fuel ash, as shown in Figs. 3 and 4. The trace element content in the fuel ash was calculated from the fuel properties, i.e. the ash and trace element content in fuel/fuel mixture. It can be seen that when coal is co-fired with SRF (i.e. without additive), the content of As, Cd, Pb, Sb and Zn in filter ash/cyclone ash increases almost linearly with their content in fuel ash, which is a strong indication that the SRF used in the experiments is quite homogeneous. Compared with the content in the fuel ash, the As, Cd, Pb, Sb and Zn content in filter ash is typically 2–5 times larger, whereas the content in the cyclone ash is usually 40–60% smaller. The observed enrichment of As, Cd, Pb, Sb and Zn elements in filter ash is qualitatively in agreement with literature, where these elements were classified as volatile trace elements in

Please cite this article as: H. Wu, et al., Trace elements in co-combustion of solid recovered fuel and coal, Fuel Process. Technol. (2011), doi:10.1016/j.fuproc.2011.05.007
pulverized coal combustion [2]. The depletion of these trace elements in cyclone ash may be primarily related with two reasons. For elements such as As and Sb, the mass balance shown in Fig. 2 is mostly around 50%. This suggests that the As and Sb content in fuel ash may be over-estimated, thus resulting in the trace element content in cyclone ash being 40–60% lower than that in fuel ash. In addition, for elements such as Cd, Pb, Sb and Zn, the content in the bottom ash collected from co-combustion experiments may be related with the physical properties of the SRF particles. The SRF particles used in the experiments are larger than the coal particles, and tend to form agglomerates during injection. As a result, the burnout degree of the SRF particles may be lower than for the coal particles in the reactor, and part of the unburnt SRF particles may end up as bottom ash with relatively high trace element content. This explanation is supported by the fact that the total amount of bottom ash collected during co-combustion experiments is increased with increasing share of SRF, and the overall burnout is decreased with higher share of SRF [12].

In comparison with the trace elements mentioned earlier, the behavior of Cr is significantly different. During co-firing coal and SRF, the Cr content in the filter ash decreases slightly with increasing Cr content in the fuel ash, whereas the Cr content in the cyclone ash. In comparison with other trace elements, the content of Cr in cyclone ash seems to be much closer to the content in fuel ash. This is probably linked to the mass balance of Cr shown in Fig. 2, which is close to or even higher than 100%. The Cr content in the bottom ash from co-combustion of coal and SRF is found to be lower than that of fuel ash. This may explain the slightly lower Cr content in cyclone ash, with respect to that in fuel ash.

The effect of additives on trace element partitioning is also illustrated in Figs. 3 and 4. The main tendency is that the Cl-based additives (NaCl or PVC) generally increase the content of As, Cd, Pb and Sb in the filter ash. This effect is particularly pronounced for the addition of 4 wt.% PVC. However, the influence of Cl-based additives on Zn and Cr is somewhat different. Most of the Cl-based additives do not have a significant impact on the Zn content in filter ash, except for the addition of 4 wt.% PVC which shows a pronounced enhancing effect. On the other hand, the Cl-based additives appear to have a reducing effect on the content in filter ash. Compared with the influence on the filter ash, the effect of Cl-based additives on cyclone ash chemical composition is generally less significant. However, a noticeable effect is that the As, Cd, Pb, Sb and Zn content in cyclone ash is lowered by the addition of 4 wt.% PVC, suggesting a promoted vaporization of these elements which has shifted the partitioning from cyclone ash to filter ash. Besides, the addition of NaCl seems to increase slightly the content of some trace elements such as Cd and Zn in cyclone ash. For Cr, it is found that most of the Cl-based additives have a promoting effect on the Cr content in cyclone ash.

Compared to Cl-based additives, the addition of kaolinite shows insignificant effect on the content of As, Cd, Sb and Zn in cyclone ash and filter ash. The addition of kaolinite significantly enriches the Pb content in cyclone ash and slightly increases the content of Pb in filter ash. For Cr, the addition of kaolinite shows a reducing effect on the content in filter ash and an enhancing effect on the content in cyclone ash. The addition of 4 wt.% ammonium sulphate generally lowers the concentration of different trace elements in filter ash. However, the impact of ammonium sulphate on the trace element content in cyclone ash is almost negligible. The results presented in Figs. 3 and 4 demonstrated the influence of additives on the trace element content in cyclone ash and filter ash. However, further discussions on the effect of additives on the partitioning of trace elements as well as the underlying mechanisms will be given in the following section.

3.3. Volatility of the trace elements

To assess the relative volatility of trace elements in pulverized coal combustion, a widely applied method is the enrichment of trace
Coal+SRF+2%PVC
Coal+SRF+2%NaCl

to trace element concentration proportional to 1/dp, whereas the is primarily due to that the gas-solid reaction mechanism would lead condensation mechanism may also result in a higher RE factor. This element is

\[ \text{RE factor} = \frac{C_i \text{ in filter ash} / C_{Al \text{ in filter ash}}}{C_i \text{ in cyclone ash} / C_{Al \text{ in cyclone ash}}} \]  

where \( C_i \) is the content of element \( i \) and \( C_{Al} \) is the content of Al.

Similar to the relative enrichment factor used in [25,26], Eq. (1) uses Al as a reference element, as Al is usually considered as an abundant and nonvolatile element with relative even distribution at different particle size. The RE factor of an element indicates whether the element is enriched (RE factor > 1) or depleted (RE factor < 1) in filter ash, with respect to the content in cyclone ash.

It should be noted that the filter ash and cyclone ash collected in the present work are separated by a cut-off diameter of 2.5 \( \mu \)m. The cyclone ash particles mostly consist of spherical particles formed by the melting of included/excluded minerals, whereas the filter ash contain both spherical particles formed by the melted minerals and nucleates generated from nucleation and coagulation of the vaporized major inorganic elements [12,13]. The trace elements vaporized during combustion would partition to the cyclone ash and filter ash through condensation and/or gas-solid reactions. Both mechanisms would favor the enrichment of trace elements in filter ash [12,21–23], and the RE factor would increase with increasing vaporization degree of trace elements. However, if the vaporization degree of a trace element is fixed, a shift from gas-solid reaction mechanism to condensation mechanism may also result in a higher RE factor. This is primarily due to that the gas-solid reaction mechanism would lead to trace element concentration proportional to 1/dp whereas the condensation mechanism would cause the trace element concentration proportional to 1/dp in the continuum regime (larger than 0.5–1 \( \mu \)m) [21–23]. Therefore, the condensation mechanism would result in a higher enrichment of trace element in small particles (around 0.5–2.5 \( \mu \)m), compared to the reaction mechanism. In addition, there are probably more particles available for condensation than for gas-solid reaction, which would further promote the enrichment of trace elements in smaller particles when the condensation mechanism is important. As a consequence, an increased RE factor of a trace element can be read as a higher vaporization degree of the trace element and/or a shift from reaction to condensation mechanism. Both influences need to be considered in interpreting the results. From a practical point of view, a higher RE factor indicates an increased partitioning of trace element to fly ash particles smaller than 2.5 \( \mu \)m. Compared with large particles, fly ash particles smaller than 2.5 \( \mu \)m generally penetrate the air pollution control system in a coal-fired power plant more easily [23]. Thus, with a higher RE factor, an increased trace element emission can be expected.

3.3.1. Volatility of Si and Cr

The RE factors of Si and Cr in different experiments are present in Fig. 5. It can be seen that the RE factors of Si are quite consistent in the experiments, being mostly between 0.7 and 0.8. The results are in line with a number of studies, showing that Si is of low volatility in pulverized coal combustion and the content of Si in submicron particles are slightly lower than that in larger fly ash particles [13,21,27]. The results also indicate that the additives do not have significant effect on the volatility of Si.

The RE factor of Cr in coal combustion is about 1.5, indicating that the volatility of Cr is only slightly higher than that of Al or Si. Similar low volatility of Cr has been observed in other studies [22,26]. When coal is co-fired with SRF, the RE factor of Cr decreases with increasing share of SRF. A similar reducing effect on the volatility of Cr has been seen when coal was co-fired with sewage sludge [4] or RDF [14]. The reduced volatility of Cr in co-firing coal and sewage sludge was attributed to the lower flame temperature in co-combustion [4]. For co-combustion of coal and SRF, it is conceivable that the flame temperature would also decrease with increasing share of SRF, as the flame temperature of a similar waste derived fuel (RDF) is found to be 200–300 °C lower than a coal flame with same excess air ratio [28]. The sensitivity of Cr vaporization to temperature has also been indicated by thermodynamic calculations [4,29]. In addition to the flame temperature, the association of Cr may also be different in the coal and SRF and has an impact on the RE factors. However, the study of trace element association in coal and SRF is outside the scope of the present work.

The RE factor of Cr is reduced with the addition of Cl-based additives, especially for 2 wt.% NaCl addition. The addition of 4 wt.% AmSulf or 4 wt.% kaolinite also appears to have a reducing effect on the RE factor of Cr, but not as significant as the Cl-based additives. For the addition of NaCl, PVC and AmSulf, it is likely that the flame temperature is further decreased compared to co-firing coal and SRF. This is because that the presence of gaseous chlorine and sulphur oxide may inhibit fuel oxidation [30], in particular the very exothermic oxidation of CO to CO\(_2\), and reduce the temperature in the reaction zone. On the other hand, thermodynamic calculations indicated that the vaporization of Cr could be significantly enhanced with a large increase in HCl concentration in the flue gas, due to the formation of CrO\(_2\)Cl\(_2\) [11]. However, such an effect is not observed in the present work, indicating the vaporization of Cr is not sensitive to the chlorine concentration in the flue gas.

In general, the results shown in Fig. 5 reveal that Cr does not have a high volatility when co-firing coal and SRF. The volatility of Cr decreases with increasing share of SRF, and is further reduced by the additives used in the experiments. This suggests that the flame temperature may be the most significant parameter for the vaporization of Cr. A relatively low flame temperature would be favorable in order to reduce the Cr vaporization/emission.

3.3.2. Volatility of Cd and Pb

The RE factors of Cd and Pb are shown in Fig. 6a. When coal is co-fired with SRF, the RE factor of Cd is in the range of 5–7, and tends to increase slightly with increasing share of SRF. The effect of the Cl-based additives is significant on the RE factor of Cd. With the addition of 1 wt.% and 2 wt.% NaCl, the RE factor of Cd is increased to about 8 and 10, respectively. With the addition of 2 wt.% and 4 wt.% PVC, the RE factor of Cd becomes about 6 and 23, respectively. In order to
further illustrate the impact of chlorine on the volatility of Cd, the RE factor of Cd from different experiments is plotted versus the RE factor of Cl in Fig. 6b (the experiments with AmSulf and kaolinite are excluded since the chlorine content in the ash from these experiments is below the detection limit). A positive correlation is found between the RE factor of Cd and the RE factor of Cl, suggesting that the partitioning of Cd is closely related with that of Cl. If the experiment with 4 wt.% PVC is excluded, the correlation is almost linear. However, in the case with 4 wt.% PVC addition, a considerably higher RE factor of Cd is obtained, which deviates from the tendency predicted by other experiments. The influence of Cl-based additives may be related with the formation of CdCl2, which is a volatile and thermodynamically favorable compound when chlorine is present in the flue gas [3,19]. Although most of the thermodynamic predictions suggest that Cd would be totally volatilized (mainly as gaseous Cd) at combustion temperatures [3,19], retention of Cd at high temperatures is observed [19], possibly related with the association form of Cd in the fuel and the limitation on the reaction time and/or mixing in a combustor. For the experiments in the present work, it may be the case that the injected Cl-based additives could react with some of the stable Cd species in the fuel and increase the overall vaporization degree of Cd. Such an effect would be particularly pronounced with the addition of 4 wt.% PVC, due to the high concentration of HCl in flue gas which may increase the reaction rates considerably.

The influence of Cl on the partitioning of Cd is qualitatively illustrated by the TEM–EDS analysis shown in Fig. 7. It is seen that when coal is co-fired with 14.8 wt.% SRF, the content of Cd in the aerosols from the vaporization mode (see Spectrum 2 and 3 in Fig. 7a) is negligible, consistent with the negligible Cl content found in these aerosols. However, when 1 wt.% NaCl or 2 wt.% PVC is added to the mixture of coal and SRF, the Cl content in the aerosols from the vaporization mode (see Spectrum 2 in Fig. 7b and Spectrum 3 in Fig. 7c) is increased significantly to about 6 wt.% and 2 wt.%, respectively. Under these conditions, despite of the small Cd content in the fuel mixture, approximately 1 wt.% of Cd is found in the vaporized aerosols. The results support that the addition of Cl-based additive may increase the vaporization of Cd during combustion, presumably related to the formation of CdCl2. However, detailed investigations on the exact chemical form of the Cd present in these aerosols are not possible from the TEM–EDS analysis.

On the other hand, with the addition of 4 wt.% ammonium sulphate, the RE factor of Cd is decreased notably, indicating a reduced vaporization degree of Cd. The injection of ammonium sulphate would greatly increase the concentration of SO2/SO3 in flue gas. Since the SO2/ SO3 would compete with gaseous chlorine for reacting with the stable Cd species in the fuel, it is likely that the formation of CdCl2 would be inhibited. The formed CdSO4 would have a lower vapor pressure than CdCl2, and this more likely to be retained in the char/ash particles. According to thermodynamic calculations [3], the presence of CdSO4 is only found at temperatures below 700 °C. However, the formation of CdSO4 at higher temperatures may be possible to occur in practical, as residence time and/or transport limitations may prevent the reactions to reach global equilibrium. The addition of 4 wt.% kaolinite also shows a slight reducing effect on the RE factor of Cd. It is most likely that part of the vaporized Cd has been reacted with the injected kaolinite particles, which are mostly particles larger than 2.5 μm. The presence of such reactions has been observed in [20], where kaolinite was found to react with vaporized Cd.

As shown in Fig. 6a, the RE factor of Pb in the range of 2–3 during co-combustion of coal and SRF, and it increases slightly with increasing share of SRF co-fired. The addition of the Cl-based additives generally enhances the RE factor of Pb, particularly for 4 wt.% PVC. Similar to Cd, the RE factor of Pb is plotted versus the RE factor of Cl in Fig. 6b. It can be seen that a positive correlation generally exists between the two factors. If the results of 4 wt.% PVC addition are not considered, the RE factor of Pb increases almost linearly with that of Cl. However, for the case with 4 wt.% PVC addition, the RE factor of Pb is higher than that predicted from the tendency of other experiments. According to thermodynamic calculations [3,19], the presence of chlorine in the combustion would favor the formation of PbCl2/PbCl, which is volatile at flue gas temperatures higher than 700 °C. Thus, it may be the case that the injection of Cl-based additives would promote the Pb vaporization via the formation of PbCl2/PbCl. Furthermore, with the addition of Cl-based additives, the distribution of vaporized Pb compounds may be shifted from PbO to PbCl2/PbCl. This transition may inhibit the reactions between vaporized Pb and coal minerals such as kaolinite [1,20,31], and cause a shift of the reaction mechanism to the condensation mechanism, which would also increase the RE factor of Pb.

The effect of Cl on the partitioning of Pb is also reflected in Fig. 7. It is seen that with a large Cl content in the vaporization mode aerosols (see Spectrum 2 in Fig. 7b), a considerable Pb content (~3 wt.%) is also found. This confirms that vaporization of Pb may be promoted by the addition of chlorine based additives, as discussed previously. However, for vaporized aerosols with negligible Cl content (see Spectrum 2 in Fig. 7a), a certain amount of Pb (~0.8 wt.%) is also observed in the aerosols. This indicates that part of the vaporized Pb may be present in other forms, such as PbO.
Contrary to the Cl-based additives, the addition of AmSulf and kaolinite both have a reducing effect on the RE factor of Pb. For the addition of AmSulf, similar explanation that has been used for Cd may be applied here, i.e. the chemical effect caused by the SO$_2$/SO$_3$ from ammonium sulphate decomposition. The lower Pb volatility during kaolinite addition is probably related with the reaction between the vaporized Pb species and kaolinite [20]. In comparison with Cd, the reducing effect of kaolinite is more significant for Pb, which is consistent with the different capture efficiency/rate found between these two trace elements and kaolinite [1,20].

The results shown in Fig. 6 suggest that Cd and Pb are highly volatile when co-firing coal and SRF, and the volatility is increased with increasing share of SRF. A most probable reason for the increased volatility is the chemical effect of the chlorine in SRF, which may promote the formation of volatile chlorides such as CdCl$_2$ and PbCl$_2$. Such effect is clearly demonstrated in experiments with Cl-based additives. The addition of ammonium sulphate and kaolinite both reduce the volatility of Cd and Pb, which is consistent with the different capture efficiency/rate found between these two trace elements and kaolinite [1,20].

3.3.3. Volatility of As, Sb and Zn

Fig. 8 shows the RE factor of As, Sb and Zn. The RE factor of As is around 5 when coal is co-fired with SRF. No obvious effect is seen for different shares of SRF. However, for the Cl-based additives, the RE factor of As is generally increased. This effect is particularly significant with the addition of 4 wt.% PVC, in which the RE factor of As becomes about 22. The increased RE factor of As during the injection of Cl-based additives is in line with other studies which found that the injection of HCl enhanced the condensation of As on small fly ashes [19]. This may be related to the formation of AsCl$_3$ (g), which is a volatile compound at combustion temperatures and could promote the vaporization degree of As [32]. Thermodynamic calculations indicate that the presence of other major inorganic elements (such as Na and K) may decrease the concentration of gaseous chlorine available for reacting with As [32]. This may explain the high volatility of As found in the injection of 4 wt.% PVC, since the effect of the major inorganic elements would become less significant in this condition and a large amount of gaseous chlorine would be available for reacting with As. For the addition of 4 wt.% AmSulf, it can be seen that the RE factor of As is reduced significantly. This result is in agreement with a study...
showing that the injection of SO₂ increased the retention of As in ash by 30% [19]. Since the sulphur retention effect was not predicted by thermodynamic calculations [19], it was suggested there may be some As compounds which have not been taken into account in the thermodynamic calculations. These compounds may have high condensation temperature and would decrease the vaporization degree of As. The addition of 4 wt.% kaolinite does not show a noticeable effect on the RE factor of As.

For Sb, it is shown that the RE factor in dedicated coal combustion is about 7.5, which is significantly higher than that in co-combustion of coal and SRF. The significant difference may be related with the association form of Sb in two fuels. It was reported that the Sb in coal is primarily associated with pyrite or organically bounded, which would be easy to vaporize during combustion [21]. For SRF, the Sb may be inorganically bounded with more stable species. However, this hypothesis needs to be confirmed by analysis of the trace element association in the two fuels, which is outside the scope of the present work. As shown in Fig. 8, the addition of NaCl does not have an obvious effect on the RE factor of Sb, whereas the addition of PVC appears to increase the RE factor. Since the addition of PVC can significantly increase the HCl concentration in flue gas, it suggests that the vaporization of Sb is enhanced in the presence of a large amount of HCl, although such effect has not been predicted by thermodynamic calculations in [33]. For the addition of AmSulf, it can be seen that the RE factor of Sb is reduced. However, the addition of kaolinite does not show an evident influence on the RE factor of Sb.

The RE factor of Zn is found to increase slightly with increasing share of SRF, when the coal is co-fired with SRF. The observation is in line with the results from co-combustion of coal with sewage sludge [24], which would be easier to vaporize than the silicates associated Zn in coal [21]. For the addition of NaCl or 2 wt.% PVC, the RE factor of Zn is slightly decreased compared to the experiment without additives. For NaCl, this may be related to the lower flame temperature in the experiment, which would adversely affect the vaporization of Zn. During the addition of 4 wt.% PVC, the RE factor of Zn is considerably increased. In this experiment, the HCl concentration in flue gas would be significant, possibly shifting the distribution of Zn from the relative stable ZnO to the more volatile ZnCl₂ [34]. The addition of kaolinite shows an insignificant effect on the RE factor of Zn. However, the addition of AmSulf provides a reducing effect, which is likely related with the possible low condensation temperature at this condition, since the chemical effect of SO₂/SO₃ would probably not be significant for the vaporization of Zn, both confirmed by experiments and thermodynamic calculations [19].

The TEM–EDS results shown in Fig. 7 may provide some indications on the partitioning of Zn at different experimental conditions. It is seen that the Zn content is considerable (>4 wt.%) in the vaporized mode aerosols from co-combustion of coal and 4.8 wt.% SRF (see Spectra 2 and 3 in Fig. 7a). Since the presence of Cl is negligible in these aerosols, the vaporized Zn species is probably present in other forms, such as ZnO. With the addition of Cl based additives, a large content of Zn can still be found in the aerosols from the vaporized mode (see Spectrum 2 in Fig. 7b and Spectrum 3 in Fig. 7c), but the Zn content in these aerosols is not much greater than that in Fig. 7a. This implies that at these experimental conditions, the effect of Cl based additives on Zn vaporization is probably limited, especially compared to the obvious effect observed on Cd and Pb.

The results presented in Fig. 8 indicate that the volatility of As and Sb is unaffected or even decreased in co-firing coal and SRF, compared to coal combustion. However, the volatility of Zn is increased in co-combustion, which is likely linked with the association of Zn in SRF. The effect of Cl-based additives on the volatility of Sb and Zn is generally not significant, but the volatility of As is increased slightly. However, in the extreme case with 4 wt.% PVC addition, the volatility of As, Sb and Zn is increased significantly. The addition of ammonium sulphate generally reduces the volatility of As, Sb, and Zn, whereas the effect of kaolinite addition is insignificant. From a practical point of view, the results imply that utilizing coal with relatively high sulphur content may be favorable for reducing the volatility of As, Sb and Zn in co-combustion. The volatility of As, Sb and Zn in co-combustion is generally not sensitive to the chlorine or aluminosilicates content in the fuel mixture, expect for the case with a very high chlorine content.

4. Conclusion

The partitioning of As, Cd, Cr, Pb, Sb and Zn in co-combustion of coal and SRF in suspension has been studied carefully in an entrained flow reactor. The influence of NaCl, PVC, ammonium sulphate and kaolinite on trace element partitioning was investigated. By analyzing the ash fractions from different co-combustion experiments, it was found that the As, Cd, Pb, Sb and Zn content in cyclone ash (fly ash particles with diameter above ~2.5 μm) and filter ash (remaining fly ash particles with diameter below ~2.5 μm) were almost proportional to their content in fuel ash, and the content in filter ash was significantly higher than that in cyclone ash. The partitioning of trace elements was influenced by additives. In general, the Cl-based additives (NaCl and PVC) enriched the content of As, Cd, Pb and Sb in filter ash, and reduced the Cr content. The addition of ammonium sulphate showed a general reducing effect on all of the trace elements in filter ash. Most of the additives had an insignificant impact on the trace element content in cyclone ash, whereas the addition of kaolinite increased the Pb content in the cyclone ash.

The volatility of trace elements was investigated by introducing a relative enrichment (RE) factor, which compared the trace element content in filter ash with that in cyclone ash. It revealed that the volatility of Cr was much lower than the other studied trace elements. The volatility of As, Cd, Pb, Sb and Zn was generally high, suggesting a large fraction of these elements was vaporized during combustion. Compared to coal combustion, the volatility of trace elements was affected by co-firing of coal and SRF. For Cd, Pb and Zn, the volatility in co-combustion of coal and SRF was slightly higher than that in coal combustion, which might promote the emission of trace elements. For trace elements such as Cd, Pb and As, the volatility was increased significantly by the addition of Cl-based additives. However, the volatility of trace elements was generally reduced with the addition of ammonium sulphur. For the addition of kaolinite, a notable reducing effect was seen on the Pb volatility, whereas the effect on other trace elements was minor.

The results from the present work imply that co-combustion of coal and SRF in a coal-fired power plant may increase the trace element content in fly ash particles greatly, primarily due to the significantly larger trace element content in SRF compared to coal. In addition, SRF may have relatively larger Cl-content and contain more organically associated trace elements than coal, which may further promote the emission of trace elements such as As, Cd, Pb and Zn, and alter the chemical form of the emitted trace elements to more volatile species such as AsCl₃, CdCl₂ and PbCl₂. An increased trace element emission together with a change of the trace element chemistry may greatly increase the toxicity of the dusts from a coal-fired power plant [35]. In order to minimize the trace element emission during co-firing coal and SRF, besides reducing the trace element content in SRF, utilizing coal with high S and aluminosilicates content and SRF with low Cl-content would be desirable.

Supplementary materials related to this article can be found online at doi:10.1016/j.fuproc.2011.05.007.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>AmSulf</td>
<td>Ammonium sulphate</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
</tbody>
</table>
ICP-OES Inductively coupled plasma optical emission spectrometry
RDF Refuse derived fuel
RE Relative enrichment
SRF Solid recovered fuel
TEM-EDS Transmission electron microscopy and dispersive X-rays spectroscopy

Acknowledgment

This work is part of the CHEC (Combustion and Harmful Emission Control) Research Centre. The present work is funded by The Technical University of Denmark, Energinet.dk and BiofuelsGS-2 (Nordic Graduate School in Biofuel Science and Technology-2). DONG Energy Power A/S is acknowledged for providing the fuels and for the fuel/ash analysis at Enstedværket Laboratory.

References