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Concentration, enrichment, and partitioning behavior of heavy metals in ash from a down-fired furnace burning anthracite coal

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Abstract: The concentrations, enrichment, partitioning behavior, emission factors and leaching characteristics of heavy metals (Pb, Cd, Cu, Zn, Ni and Cr) emitted from a 3.25 MW pilot-scale down-fired furnace burning a typically Chinese anthracite coal are studied in this study. The results show that all the six heavy metals are highly enriched in the fine fly ash, whereas they are depleted in the bottom ash. The enrichment of heavy metals increases significantly as the fly ash particle size decreases, which is found to be in the order of: Pb, Cd > Cu, Zn > Ni, Cr. A surface deposition model is developed in the study to describe the correlation between metal concentrations and particle sizes, which shows that surface reactions are the rate-limiting step in condensation of heavy metals on fly ash surface. The study also shows that the removal efficiency could exceed 98% for Cd, Cu and Ni when using an electrostatic precipitator, while it drops to 85% - 92% for Pb, Zn and Cr. In addition, the study also finds that the extractable concentrations of heavy metals in the fly ash are relatively low.
according to the leaching tests, even acids are used as the leachant.

**Keywords**: Heavy metal emission; Down-fired furnace; Anthracite; Coal combustion; Fly ash; Enrichment

1. **Introduction**

Coal is one of the most important energy resources of the world at present because it is affordable and reliable, and it is responsible for about 40% of electricity generation\(^1\). Based on the BP Statistical Review of World Energy (2016)\(^2\), despite the slight decline, 5.49 billion tons of standard coal was still consumed over the world in 2015, counting for 29.2% of the global primary energy consumption. In China, coal has been the largest primary energy source for decades, and is predicted to remain unchanged in the foreseeable future. As both the largest consumer and producer of coal in the world, China consumed 50.0% of global coal consumption in 2015, counting for 63.7% of its total primary energy consumption.

Pollutants produced by coal combustion mainly include sulfur dioxide, nitrogen oxides and particulate matter\(^3\). Moreover, various heavy metals contained in coal are also emitted into the atmosphere with exhausted gas. The concentrations of heavy metals in coal are usually quite low (typically less than 100 µg/g), so they are also called trace elements\(^4\). Most of the heavy metals are toxic and carcinogenic to human health\(^5\). Although their concentrations are very low and most of them can be removed using dust collectors with high efficiency, considerable amounts of heavy metals could be emitted because of the high rate of coal consumption. The United States Congress identified As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and radionuclides as hazardous air pollutants in the 1990 Clean Air Act Amendments. In 2011, the U.S. EPA finalized the first national Clean Air Act standards to reduce emissions of toxic metals such as Hg, As, Cr, and Ni from coal-fired power plants\(^6\). Similarly, the Europe 1998 Aarhus Protocol on Heavy Metals targets three particularly harmful heavy metals
(Cd, Hg and Pb), and the EU Directive 2001/80/EC on the limitation of emissions from large combustion plants aims to limit heavy metal emission via dust control and absorption.

There have been numerous researches on investigating the behavior of trace elements during coal combustion over the recent decades. The trace elements in coal can be categorized into three main groups regarding to their volatility behavior, as shown in Figure 1. Group 1 elements are less likely to be vaporized during the combustion, and are approximately equally distributed between the bottom ash (slag) and fly ash, showing no significant enrichment or depletion in the fly ash. Group 2 elements generally tend to be vaporized due to high combustion temperature, and subsequently condense on existing fly ash in the post-combustion zone. These elements are normally enriched in the fly ash and depleted in the bottom ash. Group 3 elements which are readily volatilized during the combustion, but are not enriched in the fly ash. Instead, they are mainly concentrated in the vapor or gas phase. However, this classification is not strict and overlaps exist. Some elements, especially Group 2 elements, may show intermediate behavior between two groups, such as Cr, Ni, U and V.

![Figure 1. Categorization of trace elements based on volatility behavior.](image)

The enrichment and partitioning behavior of trace elements in Group 2 have drawn great attention, because
most of them are toxic heavy metals. These heavy metals usually show increasing enrichment with decreasing particle size of fly ash, especially for the relatively volatile ones, such as Pb, As, Cd, Se and Zn. This notable enrichment in fine particles is unfavorable for controlling heavy metal emission via dust collectors, which are typically low-efficiency for fine fly ash (< 1-2 µm)\(^\text{12}\). On the other hand, some less volatile elements in Group 2, such as Ni and Cr, sometimes show slight enrichment in fine particles.

Besides their own volatility, studies have shown that the trace element mobility behavior is also strongly dependent on their modes of occurrence in coal, i.e. their chemical affinities\(^\text{4}\). Trace elements contained in solid fuels may be chemically bound to the organic fuel matrix, dispersed within the solid fuel particles as included mineral matter, or distributed in excluded mineral completely extraneous to the fuel particles\(^\text{9}\). In general, elements associated with the mineral matter are less likely to be vaporized, comparing with the elements showing organic affinity\(^\text{10}\). However, trace elements associated with sulfide show relatively high volatility during combustion, such as Zn, As, Se, Cd, Sn, Sb, and Pb\(^\text{13}\). The affinities of some trace elements may differ from coal to coal, and for this reason previous experimental data sometimes show significant discrepancies, such as the data for Cr and Ni.

In addition, the external combustion conditions could influence the heavy metal emission during coal combustion. These factors include combustion temperature, combustion atmosphere, coal particle size, residence times of coal particles in combustion zone, temperature profile in post-combustion zone, and so on. For example, Senior et al.\(^\text{14}\) found that flame temperature had a dramatic impact on the amount of certain trace elements such as As and Se in the submicron fly ash.

Over the past decades, a large database identifying the partitioning and emitted concentrations of a variety of heavy metals has been developed. While useful for providing average emission levels, these empirically
based models may fail when extrapolated beyond their supporting database of specific coals and power plant
types \(^{15}\). For an unknown type of combustion facility, it is always necessary to perform experimental
investigations to obtain its heavy metal emission.

Anthracite is a kind of low-volatile coal with high carbon content, which is widely used in power
generating units around the world, especially in China, North America, Europe, and Australia where reserves of
this fuel are relatively abundant \(^{16-17}\). In China, it amounts to more than 10% of total coal production \(^{18}\).
Anthracite is generally characterized with high coalification degree, low volatile, and poor reactivity, showing
difficulties in ignition and burnout. Down-fired boilers (also termed arch-fired boilers or W-flame boilers) have
been widely and successfully applied in power plants to burn anthracite with high efficiency \(^{19}\). The main
features of a down-fired boiler are 1) a high combustion temperature with assistance of refractory coverage in
the low furnace, and 2) long residence times of the pulverized coal particles in the furnace by creating W-shaped
flames. Until now, the number of down-fired boilers in China is about 130 with a total capacity over 41,000
MW, which have occupied more than 80% of the total market share in the world \(^{20}\).

The heavy metal emission from fuel combustion has been widely studied on tangentially fired
pulverized-coal boilers \(^{4, 8}\), municipal-solid-waste incinerators \(^{21}\), fluidized bed boilers \(^{22-23}\), and also
laboratory-scale drop tube furnaces \(^{24-25}\). However, no experimental data have been published on the emission of
heavy metals from a down-fired boiler which burns anthracite. Because of the high combustion temperature,
unique W-shaped flames and long residence times of coal particles in furnace \(^{26}\), the characteristics of heavy
metal emission from down-fired boilers may differ from other types of combustion facilities.

In this paper, the emission of several heavy metals (Pb, Cd, Cu, Zn, Ni and Cr) from a pilot-scale
down-fired furnace burning a typically Chinese anthracite coal is experimentally studied. The concentrations,
enrichment, partitioning behavior, emission factors and leaching characteristics of heavy metals in ash are obtained. Besides, a surface deposition model is proposed to describe the enrichment behavior of heavy metals in fly ash. The results aim to provide useful information and a reference for characteristics of heavy metal emission from widely-used down-fired boilers.

2. **Experimental Section**

2.1. **Experimental set-up and fuel**

The experimental set-up, a 3.52 MW down-fired furnace, is shown in Figure 2. The furnace is 3 m in width and 1.2 m in depth, and is surrounded by 67.27 m² water-cooled walls covered with refractory materials. Two PAX type burners (Babcock & Wilcox Company) are installed at the left and right arches of the furnace to produce W-shaped flames. A total of ten secondary air nozzles are arranged in the front and rear walls. Two forced-circulation water heat exchangers for flue gas cooling are installed both in horizontal and vertical flue gas ducts, and two tubular air preheaters are equipped at the downstream. A cyclone (type XZZ-III-D900) is used for dust removal, and there are sample points at both inlet and outlet of the cyclone.
The fuel used in this experimental study is Leiyang anthracite, which is a type of widely used Chinese anthracite coal. The proximate and ultimate analyses of the coal are given in Table 1. In the experiment, it was fed to furnace as pulverized coal particles, and the particle size distribution was: < 75 µm (72.2%), 75 - 150 µm (26.8%) and >150 µm (1%). The combustion temperature in furnace could achieve 1500 - 1600 °C, and flue gas cooled down to 160 °C at the cyclone.
Table 1. Proximate and ultimate analyses of Chinese Leiyang anthracite coal (as received)

<table>
<thead>
<tr>
<th>Proximate analysis (wt.%)</th>
<th>Ultimate analysis (wt.%)</th>
<th>(Q_{\text{net,ar}}) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_{\text{ar}})</td>
<td>(A_{\text{ar}})</td>
<td>(V_{\text{ar}})</td>
</tr>
<tr>
<td>12.61</td>
<td>18.82</td>
<td>4.75</td>
</tr>
</tbody>
</table>

2.2. Sampling method

The fly ash was sampled both at the inlet and outlet of the cyclone. The temperature, moisture and velocity of flue gas in the sample point were measured, and then appropriate nozzle diameter of the sampling probe was chosen to perform isokinetic sampling, which was important to ensure the representativeness of the sampled fly ash. The sample flow was regulated by means of an adjustable vacuum pump. Particle size distributions and mass concentration of fly ash in flue gas were obtained by a multi-stage aerosol impactor (type: WY-I), which resolved the ash sample into seven size classes. The median diameters of each stage are 14.7 µm, 9.2 µm, 6.3 µm, 4.6 µm, 3.3 µm, 2.3 µm and 1.3 µm, respectively. Prior to the impactor, a precutter cyclone was used to collect coarse particles larger than 15 µm. Meanwhile, the bottom ash was also sampled during the combustion experiment.

2.3. Analysis method of heavy metals

The concentrations of heavy metals (Pb, Cd, Cu, Zn, Ni and Cr) in coal and ash were determined using atomic absorption spectrometry (AAS) after acid digestion. For coal, prior to acid digestion, the ash sample was prepared by ashing 2 g coal in a muffle furnace at 500 °C for 4 h.

The analysis of ash samples was performed according to the Chinese National Standard DL/T 867-2004.
(Analysis methods on arsenic, cadmium, chromium, copper, nickel, lead and zinc in fly ash using atomic absorption spectrometry). Ash sample was mixed with 1 ml HCl (37 w/w%) and 3 ml HNO₃ (67 w/w%). After complete reaction, 1 ml HClO₄ (70 w/w%) and 10 ml HF (40 w/w%) were added. Then the mixture was heated on an electric heat plate at 120-150 °C until completely evaporation of water. Then, the procedure of adding acids and heating was repeated once. Next, 1 ml HNO₃ and deionized water were added to the residue. Finally, the reaction mixture was heated to accelerate dissolution, and the resolution was filtered and then analyzed by AAS.

2.4. Leaching test methods

The environmental mobility of potentially heavy metals ash is investigated by means of leaching tests. There is a wide range of standardised leaching test methods with variable complexity, reagents, temperature, agitation method, liquid-to-solid ratio and contact time, such as EN 12457-2, TCLP 1311, and ASTM D-3987. In China, there are similar National Standards which include HJ/T 299-2007 and HJ 557-2010.

In HJ/T 299-2007 test method, HNO₃/H₂SO₄ solution is used as leachant to simulate the leaching behavior of toxic elements when the ash landfill site is invaded by acid precipitation accidently. The acid solution (HNO₃:H₂SO₄=2:1, pH = 3.20) is added to the sample ash at a liquid-to-solid ratio of 10:1. After 18 hours of vibration with a speed of 30 ±2 r/min, the suspension is filtered and analyzed. The HJ 557-2010 test method uses deionized water as leachant to simulate the leachability of toxic elements when ash landfill site is eroded by underground water or surface water. The deionized water is added to the ash sample at a liquid-to-solid ratio of 10:1. Then, the suspension is vibrated horizontally at a speed of 110 r/min and an amplitude of 40 mm. After 16 hours standing, the suspension is filtered. 10 ml of concentrated nitric acid is then added to 45 ml of prepared
leaching solution. After microwave assisted digestion at 160 °C, AAS method is used to analyze the mass concentration of heavy metals, including Pb, Cd, Cu, Zn, Ni and Cr.

The comparison of some leaching test methods is shown in Table 2, demonstrating that HJ 557-2010 is similar to EN 12457-2, and HJ/T 299-2007 is similar to TCLP 1311.

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>EN 12457-2</th>
<th>TCLP 1311</th>
<th>HJ 557-2010</th>
<th>HJ/T 299-2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachant</td>
<td>Deionized water</td>
<td>Acetic acid</td>
<td>Deionized water</td>
<td>Sulfuric &amp; nitric acid</td>
</tr>
<tr>
<td>Liquid-to-solid ratio</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>pH control</td>
<td>Not a factor</td>
<td>2.88</td>
<td>Not a factor</td>
<td>3.20</td>
</tr>
<tr>
<td>Agitation time (h)</td>
<td>24</td>
<td>18</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>Room temperature</td>
<td>23</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Size distribution and micromorphology of fly ash

Most heavy metals in coal are emitted mainly in solid phase with residual ash during combustion, except few high-volatile elements such as Hg. Moreover, the heavy metals are usually enriched in fly ash, especially in fine particles. Therefore, to study the heavy metal emission, it is necessary to investigate the emission characteristics and the formation mechanisms of the fly ash.

The combustion experiment was conducted at 100% boiler load, burning Leiyang anthracite at a feeding rate of 480 kg/h. The excess air ratio was 1.2 and the peak combustion temperature in furnace was 1580 °C. The
mass size distributions of fly ash at the inlet and outlet of cyclone are shown in Figure 3. At the inlet of cyclone, the total mass concentration of fly ash is 14.1 g/m$^3$, and the mass fractions of PM$_{2.5}$ (particles < 2.5 µm in aerodynamic diameter) and PM$_{10}$ (particles < 10 µm in aerodynamic diameter) are 9.2% and 46.4%, respectively. At the outlet of the cyclone, the total mass concentration of fly ash is reduced to 2.41 g/m$^3$, and the mass size distribution changes significantly towards small size due to the low collection efficiency for fine particles. As a result, the mass fractions of PM$_{2.5}$ and PM$_{10}$ increase to 34.2% and 86.9%, respectively.

Both field and laboratory measurements as well as theoretical calculations have led to the conclusion that the fly ash emitted from coal combustion is composed of three main constituents: (1) unburnt carbon from the incomplete combustion of coal, the mass fraction of which can drop to less than 1% under good combustion conditions. In this experiment, the unburnt carbon is quite low for the high combustion temperature and long residence times of coal particles in furnace. (2) Non-volatile refractory mineral elements (such as Si, Al, Ca, Fe, etc.), which may escape the burning char and transfer into super-micrometer sized fly ash without phase change.
(solid-to-particles path). Particles which experience the melt-fusion process are usually spherical due to the
surface tension, while those particles produced by breakage of mineral matter are generally irregular. (3)
Volatile mineral elements (most alkali metals and heavy metals) that vaporize in combustion zone, and then
condense to form ultrafine particles in the post-combustion zone where the flue gas cools rapidly. Meanwhile,
the aerosol particles also grow by coagulation. The final particles may have the mean size of 1-2 µm. This
process is termed solid-vapor-particle path.

To identify the formation mechanisms of fly ash from coal combustion, the micromorphology of fly ash
sampled at the inlet of the cyclone is examined by scanning electron microscope (SEM) analysis, which is
shown in Figure 4. In the first two stages, it is found that a minority of coarse fly ash particles (> 10 µm) are
irregular, and the rest of them are spherical. At the other stages, most of the particles are almost perfectly
spherical with smooth surface, and no apparent pores on the surface. This indicates that these spherical particles
are produced mainly by the melt-fusion process of mineral matter. In addition, few aggregate particles are
observed in the SEM images.
(a) Stage 1 (>14.7 µm)  
(b) Stage 2 (14.7 µm)  
(c) Stage 3 (9.2 µm)  
(d) Stage 4 (6.3 µm)
The low combustion reactivity of anthracite coal requires high combustion temperature and long residence times of coal particles in furnace for sufficient burnout, which leads to the special design features of the
down-fired boiler, including refractory material covered furnace and W-shaped flames. According to the SEM results, the fly ash emitted from the down-fired boiler burning anthracite coal has a larger proportion of spherical particles than that produced from other types of boilers\textsuperscript{22, 30-32}. According to the mechanisms of fly ash formation, the particles produced by condensation of volatile mineral elements are mainly spherical and tend to be agglomerated, while that produced by breakage of non-volatile refractory minerals are usually irregular if the combustion temperature is low. However, the latter would become spherical due to the surface tension if they experience the melt-fusion process at a high combustion temperature. In this study, the furnace temperature is as high as 1580 °C, which is thought to be the main reason that most fly ash particles are spherical. Similarly, Yi et al.\textsuperscript{33} found that the percentage of spherical particles in the fly ash from a 220 MW anthracite-fired boiler was more than 80%. In contrast, the fly ash from circulating fluidized bed boilers was observed to be more irregular and the proportion of spherical ones in fly ash was relatively low, due to the low combustion temperature (~900 °C)\textsuperscript{22, 30}.

3.2. Concentrations of heavy metals in coal and ashes

The mass concentrations of heavy metals in coal, bottom ash and fly ash (sampled at the inlet of the cyclone) are presented in Table 3, and the literature values are also given in the table for comparison. It can be seen that the concentrations of these heavy metals in this anthracite coal are in the range of 15 - 60 µg/g, except for Cd which is quite low (0.37 µg/g). The abundances of heavy metals in coal are found to be in the order of: Zn > Cu > Cr > Pb > Ni > Cd. Comparing with the average values of Chinese coals from literature\textsuperscript{34}, the concentrations of Cu and Cr in this coal are about twice as high as the average values. However, the abundances of the heavy metals in the coal are 2-5 times as high as world average values\textsuperscript{35}, except those for Ni. The
relatively high levels of heavy metals in the anthracite may be the result of its high coalification degree.

Table 3. Mass concentrations of heavy metals in coal, bottom ash and fly ash (µg/g)

<table>
<thead>
<tr>
<th>Element</th>
<th>Coal</th>
<th>Bottom ash</th>
<th>Fly ash</th>
<th>China’s average (coal)</th>
<th>World average (coal)</th>
<th>European fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>20.6</td>
<td>28.5</td>
<td>118</td>
<td>15.55</td>
<td>7.0</td>
<td>40-175</td>
</tr>
<tr>
<td>Cd</td>
<td>0.37</td>
<td>1.45</td>
<td>2.05</td>
<td>0.24</td>
<td>0.093</td>
<td>1-6</td>
</tr>
<tr>
<td>Cu</td>
<td>37.9</td>
<td>91.1</td>
<td>214</td>
<td>18.35</td>
<td>10.8</td>
<td>39-254</td>
</tr>
<tr>
<td>Zn</td>
<td>57.0</td>
<td>139.0</td>
<td>321</td>
<td>42.18</td>
<td>12.7</td>
<td>70-924</td>
</tr>
<tr>
<td>Ni</td>
<td>16.4</td>
<td>71.6</td>
<td>89.1</td>
<td>13.71</td>
<td>11.1</td>
<td>49-377</td>
</tr>
<tr>
<td>Cr</td>
<td>31.5</td>
<td>122.0</td>
<td>172</td>
<td>15.35</td>
<td>17.6</td>
<td>47-281</td>
</tr>
</tbody>
</table>

a Average values of heavy metals in Chinese coals from literature 34.

b Average values of heavy metals in international coals from literature 35.

C Concentration ranges of heavy metals in European fly ash from literature 36.

The mass concentrations of metals in bottom ash are several times higher than that in raw coal, but they are still much lower than that in fly ash, which indicates that these metals are enriched in fly ash rather than in bottom ash. In addition, the concentrations of metals in the fly ash are basically within the range of that in European fly ash from literature 36.

Table 4 shows the mass concentrations of heavy metals in fly ash with different particle sizes. It is demonstrated that the distributions of heavy metals in fly ash are highly inhomogeneous, and their
concentrations increase substantially as the particle size decreases, showing significant enrichment in fine particles. The concentrations of heavy metals in coarse fly ash from the first stage (>14.7 µm) are similar to those in bottom ash, whereas the heavy metals in the finest particles are enriched in the range of 2 – 20 fold of that in the first stage coarse fly ash. As Group 2 elements, these heavy metals are partly vaporized to gas phase in the high-temperature combustion zone. In the post-combustion zone where flue gas cools down gradually, the vapors of heavy metals begin to condense on the surface of the pre-existing fly ash particles. Finer particles provide more surface area for condensation, which leads a much higher enrichment of heavy metals on them.

Table 4. Mass concentrations of heavy metals in fly ash with different particle sizes (µg/g)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fly ash (Diameter, µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;14.7</td>
</tr>
<tr>
<td>Pb</td>
<td>35</td>
</tr>
<tr>
<td>Cd</td>
<td>0.58</td>
</tr>
<tr>
<td>Cu</td>
<td>160</td>
</tr>
<tr>
<td>Zn</td>
<td>196</td>
</tr>
<tr>
<td>Ni</td>
<td>68</td>
</tr>
<tr>
<td>Cr</td>
<td>141</td>
</tr>
</tbody>
</table>

Pb and Cd show the most significant enrichment in fine fly ash, and the enrichment of Ni and Cr in fine particles is relatively low. The trend is basically in agreement with previous studies. According to Helble, Zn was highly enriched in the smallest ash particles, and Cr was evenly distributed for one coal, but...
increased with decreasing particle size for another.

The most important index of contamination is the mass loading of metals in different size fractions, which combines metal concentrations on a grain size basis with data on percentage of total mass, as shown in Table 5. It can be seen that the mass loading of heavy metals in fine particles is quite high considering their low mass fraction (see Figure 3). For instance, the mass fraction of PM\textsubscript{10} in fly ash is 46.4\%, while its metal mass loading is 55\% - 85\%. Furthermore, the mass fraction of PM\textsubscript{2.5} in fly ash is only 9.2\%, while its metal mass loading is as high as 16\% - 45\%. The enrichment characteristic of heavy metals in fine particles is unfavorable for controlling their emission via dust collectors, such as electrostatic precipitators (ESP) and bag filters. These dust collectors are typically low-efficiency for fine particles with size less than 1 - 2 \(\mu\)m, causing high emission of heavy metals.

<table>
<thead>
<tr>
<th>Table 5. Metal mass loadings (wt.%) in different size fraction of fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Cr</td>
</tr>
</tbody>
</table>
3.3. Enrichment behavior of heavy metals in ash

To further investigate the enrichment characteristics of heavy metals in combustion residues, the relative enrichment (RE) factor is used, which is calculated based on average contents by the equation proposed by Meij: \[ RE = \frac{C_{ia}}{C_{ic}} \times A_{ad} \] (1)

where \( C_{ia} \) and \( C_{ic} \) represent the mass concentrations of metal \( i \) in ash and raw coal, respectively. \( A_{ad} \) is the ash content in coal. RE describes the enrichment of metals in different ashes normalized to the ash content of the coal. If RE equals 1, the metal is neither enriched nor depleted in the particular ash. If RE is bigger or smaller than 1, it is enriched or depleted, respectively.

Table 6 presents the REs of PM\(_{2.5}\), PM\(_{>2.5}\) (particles >2.5 µm in aerodynamic diameter), TP (total particulate) and bottom ash. The results show that the REs of all six heavy metals are less than 1 for bottom ash, and slightly larger than 1 for fly ash. Therefore, the heavy metals are depleted in bottom ash and enriched in fly ash. In addition, the REs of PM\(_{2.5}\) are much larger than 1, indicating that the heavy metals are highly enriched in fine particles. The REs in PM\(_{>2.5}\) are a little less than 1, which means that the heavy metals are slightly depleted in coarse particles of fly ash. The enrichment of heavy metals in fine fly ash is found to be in the order of: Pb, Cd > Cu, Zn > Ni, Cr.
<table>
<thead>
<tr>
<th>Element</th>
<th>Fly ash</th>
<th>Bottom ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM2.5</td>
<td>PM2.5</td>
</tr>
<tr>
<td>Pb</td>
<td>4.34</td>
<td>0.75</td>
</tr>
<tr>
<td>Cd</td>
<td>4.90</td>
<td>0.64</td>
</tr>
<tr>
<td>Cu</td>
<td>2.91</td>
<td>0.87</td>
</tr>
<tr>
<td>Zn</td>
<td>2.95</td>
<td>0.81</td>
</tr>
<tr>
<td>Ni</td>
<td>1.82</td>
<td>0.89</td>
</tr>
<tr>
<td>Cr</td>
<td>1.91</td>
<td>0.94</td>
</tr>
</tbody>
</table>

The results in the paper are in good agreement with the previous experimental results by Querol et al.\textsuperscript{13}, which found that all these six heavy metals were enriched in fine particles, especially Cd and Pb. Ni was found to be associated with Fe, which is generally enriched in the bottom ash, so the enrichment of Ni in bottom ash is higher than other elements. In addition, Cr and Ni are also typically bound to mullite, illite and aluminosilicate glass, and are relatively difficult to volatilize during coal combustion\textsuperscript{32,40}, leading to low enrichment in fly ash. In this study, Ni and Cr are relatively less enriched in fine fly ash that other metals, but they are more enriched than that in some previous studies\textsuperscript{6,24,38,41}. The reason may be that the Cr and Ni which are mainly contained in the inorganic minerals are more volatile at high combustion temperatures\textsuperscript{30}. In addition, the long residence times of coal particles provide more chance for them to be released. Once the elements exist as gas phase, they will be enriched in the fine fly ash after the subsequent condensation.

Elements in coal can be grouped into several classes based on the enrichment behavior in coal combustion.
One of the representative classifications was introduced by Meij, as shown in Table 7. According to this classification, like most heavy metals, the six elements studied in the paper all belong to class II, but to different subclasses: Cd, Pb and Zn are grouped as class IIa; Cu and Ni are grouped as class IIb; and Cr is grouped as class IIc.

<table>
<thead>
<tr>
<th>Class</th>
<th>Bottom ash</th>
<th>Fine fly ash</th>
<th>Enrichment behavior</th>
<th>Typical elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>≈ 1</td>
<td>≈ 1</td>
<td>Not volatile</td>
<td>Al, Ca, Fe, Mg, Si, K and Ti</td>
</tr>
<tr>
<td>IIc</td>
<td>&lt; 0.7</td>
<td>1.3 ~ 2</td>
<td>Volatile, but condense on fly ash in downstream</td>
<td>Ba, Cr, Mn, Na and Rb</td>
</tr>
<tr>
<td>IIb</td>
<td>&lt; 0.7</td>
<td>2 ~ 4</td>
<td>Be, Co, Cu, Ni, P, U, V and W</td>
<td></td>
</tr>
<tr>
<td>IIa</td>
<td>&lt; 0.7</td>
<td>&gt; 4</td>
<td>As, Cd, Ge, Mo, Pb, Sb, Ti and Zn</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>≪ 1</td>
<td>≈ 0</td>
<td>Volatile, nearly no condensation</td>
<td>B, Br, C, Cl, F, Hg, I, N, S and Se</td>
</tr>
</tbody>
</table>

Comparing with Table 6 and Table 7, it can be seen that the enrichment behavior of heavy metals from this down-fired furnace burning anthracite coal is essentially coincident with Meij’s classification. Nevertheless, in this study Ni is grouped as class IIb rather than IIc for the relatively low RE. Similarly, Zn is grouped as class IIb rather than IIa. The discrepancies could be due to the different modes of occurrence of heavy metals in coal and the combustion conditions.

In particular, it is generally considered that Cr is hard to be classified for its various modes of occurrence in coal. If associated with mineral matter, it is less likely to vaporize during coal combustion. While when associated with organic parts of coal, it is more likely to vaporize and shows enrichment behavior. In some other
studies, Cr was found to be not enriched and classified as class I \cite{8, 43}. In this study, the enrichment of Cr in fine fly ash is apparent. In addition to the modes of occurrence in coal, high combustion temperature in the down-fired furnace could be another reason, which increases the volatility of Cr.

REs of heavy metals in fly ash with different particle sizes are shown in Figure 5. The REs of these elements in coarse particles (> 10 µm) are generally less than 1, which are very similar to that observed by Haynes et al. \cite{44}. REs increase rapidly as the particle size is decreased, and reach about 6 for Pb and Cd in the finest particles (~ 1.3 µm). The REs of Ni and Cr in fine particles are relatively low, however the trend that the enrichment increases with reducing particle size is still very obvious.
3.4. **Surface deposition model for heavy metal enrichment**

During coal combustion, mineral matter in coal transfers into fly ash via various paths. The behavior of heavy metals which are termed trace elements due to their extremely low concentrations in coal, differs from that of main composition of fly ash (refractory minerals). In general, a major portion of heavy metals in coal is vaporized in combustion zone, while some metals are remained in the minerals as solid phase. It is worth noting...
that the reducing atmosphere near the surface of the burning coal particles typically enhances evaporation of heavy metals from coal matrix. The refractory minerals are less like to be vaporized, and transfer into fly ash mainly by breakage, melting, fusion, solidification and coagulation. Only a minority of refractory minerals and alkali metals is vaporized and then forms fine fly ash via condensation and agglomeration. Minerals in coal begin to form fly ash when flue gas leaves the high temperature combustion zone. The fusion and condensation of refractory oxides occur prior to the heavy metal vapors due to their high melting points, constituting the major components of fly ash. In the post-combustion zone where flue gas cools down gradually, the vapors of heavy metals, most of which belong to class II, begin to condense. Moreover, oxidation of the metals in the gas phase may also result in the critical supersaturation and condensation, without necessarily requiring a sharp temperature drop.

The heavy metal vapors may transfer to ultrafine fly ash particles by homogeneous nucleation, or deposit on the surface of the existing fly ash particles via heterogeneous condensation. The latter process is always dominant for the following reasons: (1) The heavy metals in the coal matrix are usually in trace amounts. Even if all the metals are transferred to the gas phase, the concentrations will typically be much lower than the saturation concentrations of the metals or metal oxides required for homogeneous nucleation. In contrast, the heterogeneous condensation of metal vapors require much lower concentrations. (2) The pre-existing fly ash particles entrained in the flue gas contribute massive available nuclei, which significantly promotes heterogeneous deposit of metal vapors on their surface.

Based on the above analysis, the fly ash particles from coal combustion are mainly composed of refractory oxides (e.g., Fe, Mg, Si, Al, Ca), and covered with heavy metal components on their surface. In fact, this distribution pattern has been verified in previous studies. Lind et al. found that the major component of
submicron particles were SiO$_2$, MgO, CaO, and FeO, despite the enrichment of the trace elements. Bhanarkar et al. $^{48}$ also demonstrated that ash particles with sizes of 0.01 – 0.1 µm were primarily formed via vaporization and condensation of major elements in coal such as Si and Fe. The SEM analyses of individual argon ion etched fly ash particles showed that heavy metals such as Zn, Cr, and Ni predominated on particle surfaces $^{49}$. In addition, the study of Haynes et al. $^{44}$ indicated that the involatile core of the residual ash particles (CaO, Al$_2$O$_3$, MgO, SiO$_2$, and Fe$_3$O$_4$) was coated with a deposit of some volatile heavy metals, and the core itself was depleted of these surface-enriched species.

In conclusion, the heavy metal $i$ in fly ash particles is considered to be constituted by: 1) the non-vaporized portion which remains in the coal matrix and disperses in the ash cores; and 2) the surface-enriched portion which condense on the particle surface via gas-to-particle conversion in post-combustion zone. A surface deposition model can be constructed to describe the concentration of the heavy metal $i$, $C_{ia}$, in a fly ash particle, which is given by $^{49}$

$$C_{ia} = C_{i0} + \frac{C_{is}S}{\rho_pV}, \quad (2)$$

where $C_{i0}$ is the mass concentration of metal $i$ which is not vaporized and distributed throughout the particle. $C_{is}$ is the deposition rate of metal vapor $i$ on the particle surface. $S$ and $V$ are the surface area and volume of the particle, respectively. $\rho_p$ is the density of the particle. By assuming that the particle is perfectly spherical with a diameter of $d$, equation (2) can be rewritten as

$$C_{ia} = C_{i0} + \frac{6C_{is}}{\rho_p d}. \quad (3)$$

By assuming that $C_{i0}$, $C_{is}$ and $\rho_p$ are constants, the concentrations of heavy metals are then inversely proportional to the fly ash particle diameter. Consequently, the validity of the proposed model can be tested by
examining the linearity dependence of $C_{ia}$ on $d^{-1}$.

Furthermore, the vaporized fraction of the total metal element, $\varphi_i$, is given by

$$\varphi_i = 1 - \frac{C_{i0}}{C_{ia}}. \quad (4)$$

Meanwhile, the thickness of deposition layer of element $i$ can be roughly estimated as

$$l_i = \frac{C_{is}}{\rho_i}, \quad (5)$$

where $\rho_i$ is the deposition layer density of the component of element $i$ on the particle surface.

The plots of mass concentrations of heavy metals in fly ash versus $d^{-1}$ are shown in Figure 6. The experimental results are presented as scattered points, and the solid straight lines in the figure represent the linear fitting of the data. Then, by assuming $\rho_p = 2.4 \text{ g/cm}^3$ and $\rho_i = 3 \text{ g/cm}^3$, the parameters derived from the surface deposition model are listed in Table 8. Good linear correlations between mass concentrations and $d^{-1}$ are observed in Figure 6, with high correlation coefficients (>0.9), for all the six heavy metals. This indicates that the proposed surface deposition model is suitable for describing the enrichment behavior of heavy metals in fly ash emitted for the down-fired furnace burning anthracite coal that is discussed in this paper. In addition, the estimated thicknesses of deposition layers of these heavy metals are 0.02 - 1.7 Å, which are considered reasonable for the deposition and adsorption process.
Figure 6. Dependence of heavy metal concentrations in fly ash on $d^{-1}$. 
Table 8. Parameters derived from the surface deposition model

<table>
<thead>
<tr>
<th>Element</th>
<th>$C_0$, µg/g</th>
<th>$C_s$, µg/cm$^2$</th>
<th>Linear correlation coeff.</th>
<th>Deposition layer thickness, Å</th>
<th>Vaporized fraction, $\varphi_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>16.08</td>
<td>0.032</td>
<td>0.985</td>
<td>1.06</td>
<td>86.4%</td>
</tr>
<tr>
<td>Cd</td>
<td>0.00</td>
<td>0.00065</td>
<td>0.979</td>
<td>0.023</td>
<td>100.0%</td>
</tr>
<tr>
<td>Cu</td>
<td>82.47</td>
<td>0.035</td>
<td>0.990</td>
<td>1.17</td>
<td>61.4%</td>
</tr>
<tr>
<td>Zn</td>
<td>161.2</td>
<td>0.050</td>
<td>0.972</td>
<td>1.67</td>
<td>49.8%</td>
</tr>
<tr>
<td>Ni</td>
<td>71.7</td>
<td>0.0060</td>
<td>0.945</td>
<td>0.20</td>
<td>19.6%</td>
</tr>
<tr>
<td>Cr</td>
<td>129.6</td>
<td>0.013</td>
<td>0.980</td>
<td>0.43</td>
<td>24.7%</td>
</tr>
</tbody>
</table>

Good linear correlation between metal concentration and $d^{-1}$ was also obtained by Senior et al. 14. In their experimental study, the concentrations of As and Se in the super-micron particles were better correlated with $d^{-1}$ than $d^{-2}$, especially at high flame temperature. Moreover, Haynes et al. 44 found that the particle diameter dependence of the concentrations was much better expressed by the $d^{-1}$ relationship than $d^{-2}$, for all the studied elements (As, Sb, K, Mn, V and W), apart from Na.

In some other studies, however, no such relationship was found. In a study of circulating fluidized-bed coal combustion 31, none of the elemental concentrations showed $d^{-n}$ dependence. One of the possible reasons was that the fly ash particles were irregular in shape due to low combustion temperature, as equation (3) is based on the assumption that the particles are perfectly spherical. In the study by Haynes 44 which obtained $d^{-1}$ dependence for most elements, measurements of the specific surface area of fly ash agreed with that predicted for hard spheres, indicating that the particles were basically spherical with negligible porosity.
In our experiment, the combustion temperature of the down-fired furnace burning anthracite coal is as high as 1580 °C, which is generally higher than that of circulating fluidized-bed boilers, tangentially fired pulverized-coal boilers, and municipal solid waste incinerators. Besides, the residence times of pulverized coal particles are prolonged due to the unique W-shaped flames. As a result, the fly ash particles are mainly in the shape of hard spheres with smooth surfaces and negligible porous microstructure (see SEM images in Figure 4), which is in good agreement with the assumption of equation (3). This is one of the important reasons for the good linear relationship between heavy metal concentrations and reciprocal of particle diameters.

The conversion of vaporized heavy metals into various solid forms deposited on the surface of the pre-existing fly ash is complex, including physical diffusion and chemical transformation \(^{10}\), which has been discussed by Friedlander \(^{47}\) as follows. (1) For heterogeneous condensation by physical diffusion, the concentrations of the volatile metals follow \(d^{-n}\) dependence, \(n=1\) or 2. In the continuum regime, where particles are much larger than the mean free path of molecules (Knudsen numbers, \(Kn \ll 1\)), the gas-to-particle conversion is controlled by continuum film diffusion, then the concentrations of heavy metals in particles show \(d^{-2}\) dependence. In the free molecular regime for very small particles \((Kn > 1)\), the dependence would be expected to be \(d^{-1}\) as the controlling mechanism is free molecular film diffusion. (2) For surface-reaction controlled deposition, the concentration of metals always show \(d^{-1}\) dependence, despite the particle size range.

Under our experimental conditions (atmospheric pressure, 150-1600 °C), the mean free path of molecules is calculated to be approximately 0.1 - 0.5 µm, so the fly ash particles with sizes of 1 – 15 µm are in the continuum regime \((Kn \ll 1)\). Therefore, the possible mechanisms could be continuum film diffusion or surface-reaction controlled deposition. Since the heavy metal concentrations show strong \(d^{-1}\) dependence, it is
concluded that surface reactions are the rate-limiting step in condensation of these metals on fly ash surface.

Physical condensation mechanisms (continuum and free molecular) occur when the temperature is below the metal vapor dew point. However, chemical reaction can occur at any temperature far above the dew point, and this facet is especially relevant to trace metals in coal, where trace metal concentrations are very low and dew points may also be quite low \(^9\). In fact, the vapor of heavy metals and their compounds will react with some major mineral components of coal fly ash, such as CaO, SiO\(_2\), and Al\(_2\)O\(_3\). Chen et al. \(^{50}\) found that chemical reactions were the major adsorption mechanisms of several heavy metals. For example, Cr would react with CaO to form thermostable product CaO\(\cdot\)Cr\(_2\)O\(_3\)(s); Pb and Cd could react with SiO\(_2\) to form metal silicate PbSiO\(_3\)(s) and CdSiO\(_3\)(s). Querol et al. \(^{13}\) also revealed that CaSO\(_4\) and CaO had a high sorption capacity for some heavy metals.

The vaporized fractions of the heavy metals are presented in Table 8. The results show that Pb and Cd are vaporized in a considerably large proportion (85% - 100%), followed by Cu and Zn (50% - 60%). The vaporized fractions of Ni and Cr are relatively low (20% -25%), accordingly the REs of the two elements are relatively high (>0.7).

The volatility of heavy metals strongly depends on the chemical properties of their compounds in flue gas. Based on equilibrium calculations \(^{51}\), Cd existed mainly in gas phase as Cd(g) and CdO(g) above 1000 K, and Cd(g) accounted for more than 90% (mol/mol) of the Cd. PbO(g) was the major stable Pb-species above 1300 K, which gradually decomposed to Pb(g) with increasing temperatures above 1500 K \(^{39}\). According to Senior et al. \(^{25}\), it was found that 50% - 90% of Zn was vaporized during the combustion of pulverized coal.

As a comparison, Ni was the predicted solid species below 1600 K, and only approximately 17% (mol/mol) of Ni was vaporized mainly as NiO(g) above 1700 K, according to the equilibrium calculations \(^{39}\). Cr was
predicted to exist as solid phase at 1423 K, under either oxidizing or reducing conditions.\(^{25}\) The volatility of Cr will increases only if it is associated with the organic matter or sulfides. In another study on pulverized combustion of bituminous coal, vaporized mass fraction of Cr was only 20\%.\(^ {52}\)

Besides, the volatility of heavy metals is also influenced by the modes of occurrence in coal. The elements of Cd, Pb and Zn, which have a strong affinity for sulfur, are regarded as being mostly volatized during combustion because they occur as sulfides or within sulfide minerals. This is the result of the high temperature and reducing conditions near the surface of a burning coal particle which breaks the chemical bonds between metallic elements and sulfur in the sulfides. On the other hand, Cr and Ni are typical elements which have a strong affinity for oxygen and are usually associated with mullite or aluminosilicate minerals, so they are less likely to be vaporized during coal combustion\(^ {10,32}\). The experimental results are similar to Helble’s study\(^ {24}\), in which only a small fraction of Cr was vaporized during the combustion of sub-bituminous coal, and the majority of it was either retained by aluminosilicate minerals, or was initially present in a more refractory form.

3.5. **Partitioning behavior of heavy metals in combustion products**

The partitioning behavior of heavy metals in different combustion products, e.g. bottom ash, fly ash and flue gas, is also investigated. The concentrations of heavy metals in flue gas are determined by the mass balance method using the following equation: \( M_{ic} = M_{if} + M_{ib} + M_{ig} \), where \( M_{ic}, M_{if}, M_{ib}, \) and \( M_{ig} \) represent the element \( i \) content in coal, fly ash, bottom ash and flue gas, respectively.\(^ {33}\) In addition, it is assumed that the produced ash comprises of 10\% bottom ash and 90\% fly ash, according to empirical data.\(^ {38}\)

The calculated results are illustrated in Figure 7, which shows that the heavy metals emitted from coal combustion are mainly distributed in fly ash (80\% - 95\%). The mass percentages of Pb, Cu and Zn in bottom ash.
ash are relatively low (less than 5%), while the elements of Cd, Ni and Cr have larger proportions in bottom ash (10% - 13%). Good mass balance closure of the elements of Cd, Cu, and Ni is obtained by summing their mass contents in bottom ash and fly ash, indicating that the condensation of the metal vapors is complete for these elements at the post-combustion zone. However, the mass balance shows that the condensation of Pb, Zn and Cr is not complete and small fractions of Pb and Zn still exist in the gas phase. In particular, the percentage of Pb in gas phase is as high as 14%. This is unfavorable for controlling heavy metal emission via dust collectors, which are ineffective for removal the gaseous metals in flue gas. The partitioning behavior of heavy metals observed in this study generally corresponds to the levels of results presented in previous studies. Swanson et al. investigated two coal-burning power plants in the United States, and found that the percentage of Pb in flue gas was in a range of 30% - 50%. They also found that the percentage of Cr in flue gas was around 10% in some cases.

Figure 7. Mass percentages of heavy metals in bottom ash, fly ash and flue gas.
3.6. Emission factors of heavy metals

In this study, the experimental set-up is a pilot-scale down-fired furnace, which is equipped with a low-efficiency cyclone for dust separation. In industrial applications, large-scale commercial down-fired boilers are typically equipped with high-efficiency ESPs. In order to better evaluate the emission, the controlled emission factors of heavy metals given in the paper are calculated based on the collection efficiency of a ESP applied in an industrial application.

To do this, the collection efficiency of a typically ESP equipped by a 300 MW down-fired boiler was measured using the aerosol impactor (type: WY-1), which is presented in Table 9. It can be seen that the total collection efficiency of the ESP is 99.65%, but it declines as particle size decreases. For PM$_{2.5}$, the collection efficiency is reduced to 97% approximately. The collection efficiency for total particles and fine particles is in good agreement with the experimental results by Meij$^{12}$ and Bhanarkar et al. $^{48}$.

Table 9. Collection efficiency of the ESP for different sized particles

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>&gt;14.7</th>
<th>14.7</th>
<th>9.2</th>
<th>6.3</th>
<th>4.6</th>
<th>3.3</th>
<th>2.3</th>
<th>1.3</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection efficiency(%)</td>
<td>99.98</td>
<td>99.98</td>
<td>99.93</td>
<td>99.80</td>
<td>99.57</td>
<td>98.95</td>
<td>97.57</td>
<td>96.68</td>
<td>99.65</td>
</tr>
</tbody>
</table>

Based on the measured collection efficiency of the ESP, the emission factors of heavy metals from the down-fired boiler can be determined, combined with the mass size distribution of the fly ash, concentrations and distribution of metals in different sized particles. The results are listed in Table 10. For the elements of Cd, Cu, Ni and Cr, which are almost totally emitted as solid phase, the removal efficiency is 96% - 99%. However, it is still lower than the total collection efficiency of TP. For Pb and Zn, the removal efficiency is relatively low (85%
- 92%) since a small portion of them exist as gas phase in the flue gas, which cannot be removed by the ESP.

The heavy metal emission factors from coal combustion in worldwide are also given in Table 10. It is shown that the emission factors of Cd, Cu, Ni and Cr, controlled by the ESP, are lower than the worldwide ranges, attributing to the high collection efficiency of the modern ESP.

<table>
<thead>
<tr>
<th>Element</th>
<th>Uncontrolled emission factor</th>
<th>Removal efficiency</th>
<th>Controlled emission factor</th>
<th>Worldwide range b (µg/MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/t coal (µg/MJ)</td>
<td>g/t coal</td>
<td>µg/MJ</td>
<td>g/t coal</td>
</tr>
<tr>
<td>Pb</td>
<td>20.0 848.2</td>
<td>85.53%</td>
<td>2.90</td>
<td>122.7</td>
</tr>
<tr>
<td>Cd</td>
<td>0.35 14.7</td>
<td>98.58%</td>
<td>0.005</td>
<td>0.21</td>
</tr>
<tr>
<td>Cu</td>
<td>36.2 1533.2</td>
<td>99.15%</td>
<td>0.31</td>
<td>13.1</td>
</tr>
<tr>
<td>Zn</td>
<td>54.4 2300.2</td>
<td>92.09%</td>
<td>4.30</td>
<td>181.8</td>
</tr>
<tr>
<td>Ni</td>
<td>15.1 638.8</td>
<td>99.42%</td>
<td>0.09</td>
<td>3.7</td>
</tr>
<tr>
<td>Cr</td>
<td>29.2 1234.0</td>
<td>96.42%</td>
<td>1.04</td>
<td>44.2</td>
</tr>
</tbody>
</table>

a Controlled by the ESP with collection efficiency listed in Table 9.

b From literature 53.

3.7. Leaching of heavy metals

To evaluate the leaching behavior of fly ash in landfill under various conditions, the leaching tests were conducted using HJ/T 299-2007 and HJ 557-2010 methods (see Table 2). The results are presented in Table 11. The extractable percentages of these six heavy metals are quite low (<1%), when deionized water is used as leachant. The pH value of leachant has a strong influence on leaching behavior. The heavy metals show higher
extraction proportions (3% - 10%) when using acids as leachant. Zn has the highest extraction percentage and concentration, while Cr has the minimal ones. It is worth noting that the extractable percentages of these heavy metals are all of relatively low level. The relative insolubility of these metals from the coal fly ash could be the result of the mineral nature of coal ash and large quantities of Si, Al, and Ca that are known to interact with trace metals to form relatively insoluble alumina, silica and calcium complexes. The extractable concentrations of the six heavy metals are all below the limits of Chinese National Standard GB 5085.3-2007.

<table>
<thead>
<tr>
<th>Element</th>
<th>HJ/T 299 Concentration</th>
<th>Extractable percentage</th>
<th>HJ 557 Concentration</th>
<th>Extractable percentage</th>
<th>China limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.77</td>
<td>6.5%</td>
<td>0.059</td>
<td>0.50%</td>
<td>5</td>
</tr>
<tr>
<td>Cd</td>
<td>0.012</td>
<td>5.7%</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>0.75</td>
<td>3.5%</td>
<td>0.11</td>
<td>0.52%</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>3.63</td>
<td>11.3%</td>
<td>0.29</td>
<td>0.90%</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>0.77</td>
<td>8.6%</td>
<td>0.037</td>
<td>0.42%</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.57</td>
<td>3.3%</td>
<td>0.11</td>
<td>0.61%</td>
<td>15</td>
</tr>
</tbody>
</table>

n.d. = not determined.

* Chinese National Standard GB 5085.3-2007 (Identification standards for hazardous wastes)
4. Conclusions

The concentrations, enrichment, partitioning behavior, emission factors and leaching characteristics of heavy metals (Pb, Cd, Cu, Zn, Ni and Cr) emitted from a 3.25 MW pilot-scale down-fired furnace burning a typically Chinese anthracite coal are studied.

(1) All the six heavy metals are highly enriched in the fine fly ash, and the enrichment increases significantly as the particle size decreases. The enrichment of heavy metals in fine fly ash is found to be in the order of: Pb, Cd > Cu, Zn > Ni, Cr. Whereas the REs of metals in bottom ash are all less than one. Comparing with other types of boilers, the enrichment of Ni and Cr in fine particles emitted from the down-fired furnace is higher.

(2) Good linear correlations between metal concentrations and $d^{-1}$ are observed, which can be well explained by the proposed surface deposition model. One of the main reasons is that the fly ash particles are mainly in the shape of hard spheres with smooth surface and negligible porous microstructure, due to the high combustion temperature and long residence times of coal particles in the down-fired furnace. The $d^{-1}$ dependence found in the experiment shows that surface reactions are the rate-limiting step in condensation of heavy metals on fly ash surface.

(3) The heavy metals emitted from coal combustion mainly exist in fly ash (80% - 95%). Most of Cd, Cu and Ni is only distributed in the bottom ash and fly ash, and their removal efficiency by the ESP is above 98%. For Pb, Zn and Cr, which partly exist in the gas phase in flue gas, the removal efficiency using the ESP is reduced to 85% - 96%.

(4) The extractable concentrations of heavy metals in fly ash are relatively low and below the limits of Chinese National Standard, even use acids as leachant.
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