Measurement of mercury and trace element emissions from coal combustion boilers

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Abstract

In the combustion process for fossil fuel and waste materials, many environmental impacts with SOx, NOx and particulate were reduced by developed flue gas cleaning equipments and legally controlled. Although it appears that trace elements are not currently a major issue for the coal industry, the trends of more stringent environmental regulations in Europe and USA gives the necessity to control the emissions of the trace elements into atmosphere and to understand the state of emissions and the mechanism of formation and emission in combustion processes. We measured emissions of the trace elements from industrial boilers in coal utilization facilities with different types of combustion boiler and flue gas cleaning equipment. As a result, the relationship between those emissions and operating conditions or flue gas cleaning conditions suggested that those concentrations at the stack were strongly dependent on the flue gas temperature or the equipment. However, the fate of volatile metals, especially mercury, should be comprehensively discussed from the balance in processes.

1 Introduction

Most elements in the periodic table are contained in coal, which are released by combustion and emitted on or in particulate and in vapor form. If coal consumption were to be significantly increased, although concentration of trace elements in coal is very low, the effects of toxic trace elements on human health...
and the external environment exposed would be of concern. Legislation on trace elements has not, however, involved their specific controls within the coal industry anywhere [1]. There is a trend towards condensation into fine particles and, consequently, some trace elements can occur in higher concentrations in the solid residues, which could pose problems in their disposal, utilization and potential impact of emissions of trace elements to the atmosphere, adsorbed on the finest particles. Since we experienced air pollution problems in Japan in the 1960s, pollutant emissions such as sulfur oxides (SOx), nitrogen oxides (NOx) and particulates are seriously controlled by electrostatic precipitator (EP), flue gas desulfurization (FGD), and selective catalytic reduction of NOx (SCR). This environmental equipment should be available to reduce trace elements. It is tacitly assumed that existing particulate emissions standards are sufficient to control trace element emissions. In order to understand the fate of these elements in modern coal combustion, investigations have been carried out and are now in progress in Japan.

In this study we investigated the behavior and the mass balance in industrial coal combustion plants, and difference of the enrichment factor for types of coal combustion boilers, flue gas cleaning systems, and flue gas desulfurization. We report here the following elements; Al, As, Br, Be, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, Mg, Mn, Ni, P, Pb, Se, Si, Sn, V, Zn. Then, we investigated the effectiveness of conventional flue gas control equipment to reduce the trace element emissions from stack and the fate of those.

The term of trace elements is referred in this paper to cover the minor elements.

### 2 Coal combustion processes

Toxic trace elements in flue gases and on ash particles emitted into the atmosphere from coal-fired power stations, at three locations in Japan, were already reported by CRIEPI [2]. In this study on the effectiveness of flue gas control system, we investigated the behavior of the 23 trace elements at the exit of the boiler, de-NOx control, particulate control, and de-SOx control equipment installed into industrial coal-fired plants. The difference of seven plants we measured is shown in Table 1.

| Plant-1 | Bubbling FBC | Small | Bag house | Non | In bed |
| Plant-2 | PC | Middle | EP | Non | Non |
| Plant-3 | PC | Large | EP | SCR | Mg(Ca(OH))2 |
| Plant-4 | PC | Small | EP | Non | Mg(OH)2 |
| Plant-5 | PC | Large | EP | SCR | Mg(OH)2 |
| Plant-6 | PC | Small | Baghouse | Non | Non |
| Plant-7 | Circulating FBC | Middle | Baghouse | Non | In bed |

*: Small, Middle, and Large are respectively about 10 to 20 t/h, 20 to 30 t/h and more than 30 to 60 t/h of coal feed rate.
Figure 1: A typical process of pulverized coal combustion boiler.

Figure 1 shows a typical temperature distribution of pulverized coal combustion process (PC). Others are bubbling and circulating fluidized bed boiler processes (FBC). Flue gas cleaning equipments are; electrostatic precipitators (EP) and fabric filters (baghouse) as particulate control, wet de-SOx scrubbers as flue gas desulfurization (FGD), and selective catalytic reduction (SCR) as NOx control (de-NOx). Sampling of gas and solid ash was conducted at the exit of each of flue gas control. The sampling method based on the Japan Industrial Standard (JIS) was used to determine the particulate mass loading and to collect solid and vapor phase samples of the flue gas. Particulate matter was collected on a quartz fiber filter and the vapor phase species were absorbed in an impinger train (JIS Z8808). The measured items were wet gas volume (JIS Z8808), dry gas volume, flue gas temperature (JIS Z8808), sampling of trace elements in flue gas (Br (JIS K0085-6.1), Hg (JIS K0222), F(JIS K0105), others(JIS K0083)), SOx (JIS K0103), NOx (JIS K0104), HCl (JIS K0307), particle size distribution and particulate matter concentration (JIS Z8808). For environmental assessments of trace element emissions, it is useful to know the concentrations in coals. The relationship between elements in coals and in emissions were investigated. This aspect lies outside the objective of this paper and it will be reported at another opportunity.

3 Measurement results

3.1 Emissions

In this study we classified trace elements into five groups, which has been cited by many researchers according to their partitioning in a pulverized coal-fired power plant. Group-1 elements are those of no or very low volatility even at high combustion temperature between 1200 and 1600°C. Group-2 is lower volatility dependent on the coal type and the combustion temperature. Group-3 is vaporized but then recondensed, tending to concentrate in or on the fines at lower temperature in flue gas equipment. Group-4 elements remain mostly in
the gas phase and may be emitted from the stack. Group-5 is of halogen elements.

- (1) Non volatile: Al, Si, Ca, Mg, Mn, Co, Cr
- (2) Semi-volatile: Fe, Cu, P, Ni, Be
- (3) Semi-volatile: Zn, Pb, Cd, Sn, V, As
- (4) Volatile: Se, Hg
- (5) Halogen: Br, F

3.2 Mass balance

Trace elements in coal into combustor are melted or vaporized and condensed into bottom ash, fly ash, and particulate dust. Figure 2 shows the balance of each element with measured plants. The balance was defined by the following equation:

\[
\text{Mass balance} = \frac{\text{Output of trace element by mass flow rate (mg/l h)}}{\text{Input of trace element by mass flow rate (mg/l h)}} \times 100
\]

It is very difficult to be completely recovered as shown in Fig. 2. Investigation on trace element emissions seeks to account for trace elements in all input and output streams. The sampling and analytical techniques are very complex and the results include the uncertainties. Then, although we must consider the use of range values and standard deviations, we focused on the overall contributions of flue gas cleaning system in coal-fired plant to the stack emissions and to the characteristics of the coal residues. Therefore, for the elements over 100%, assuming to be 100% recovery and to keep the composition, we corrected the mass balance, and for the elements below 100%, unknown percentage are remained. Based on these modification, the percentage of trace elements in the bottom ashes, in the fly ashes and in the stack emissions are shown in Figs. 3(a),

\[\text{Figure 2: Mass balance of trace elements without modification.}\]
3(b) and 3(c), respectively. From Fig. 3(a) of bottom ash, it can be seen that the group-I elements are recovered by less than 10% for PC boiler without plant-I and more than 10% to 25% for bubbling FBC. The fraction of recovery of elements is decreased with higher volatility, to group-3, 4 and 5. However, group-1 and 2 elements in plant-1 of the FBC operated at lower combustion temperature keep the relatively high percentage. It suggests that trace elements into the bottom ash are dependent on combustion temperature rather than coal type. Figure 3(b) shows percentages of the elements recovered in fly ash. Group-I elements are recovered by more than 75% from fly ashes and almost 100% by adding this to the recovery from bottom ashes. One of the reasons for the low recovery of plant-4 may be low mass balance of the element as shown in Fig. 2. Then, without the plant-4, the behavior of group-1 is almost similar to each of other plants. For some elements of group-2 with semi-volatile elements, the plant-3 and 5 with a large-scale and with NOx control equipment appears to give higher recovery by fly ash than without NOx control, whilst the trend for group-3 and 4 is reversed and the recovery ratio is generally decreased. The higher recovery of plant-6 for these group elements should be due to baghouse or fabric filter. It suggests that the fabric filter can be more available to capture particulates with trace elements than the electrostatic precipitator. Furthermore, the percentages of recovery of Hg, Br and F of group-4 and 5 become below 20% for pulverized coal combustion processes. The results of FBC give considerably higher recovery even for Hg and F. This means that the FBC process with bed material and operating at low temperature is an excellent low emission system for the trace elements. Additionally, if the trace elements would pass through the particulate control, then such Hg should be emitted to the atmosphere.

Figure 3(c) shows the percentages of elements recovered from stack gas. Without any effort to reduce these emissions, the elements are emitted from the stack to the atmosphere. Sn, Hg, and Br of group-4 and 5 for plant-1 and further F for plant-2 were emitted. A common reason for the plant-1 and 2 is because those plants have not any wet de-SOx equipment or no FGD system after particulate control device. It suggests that the wet FDG to reduce SOx is available also to reduce volatile elements.

It can be seen from above partitioning of trace elements that these are mainly captured by coal fly ash or FBC sorbents in particulate control equipment but some elements escaped it can be captured by wet scrubbing equipment.

3.3 Enrichment factor

Figures 4(a) and 4(b) for an example of plant-2 show relationships of concentrations of each trace element between in coal and in bottom ash and between in coal and in fly ash, respectively. Some elements in ashes appear to be condensed if comparing with the concentrations in coal. However, coal contains combustible hydrocarbons fired out and then condensation accounted as enrichment of trace elements in coal would be overestimated. To understand
Fig. 3(a), 3(b) and 3(c) Percentages of trace elements in particulate recovered as bottom ash (a), fly ash (b) and dust in stack gas (c)
Fig. 4(a) and 4(b): Relationships of concentrations of each trace element between coal and bottom ash (a) and between coal and fly ash (b).

the effects of combustion on trace element release from coal, we must investigate about the differences in combustion temperature, excess air, residence time and enrichment of differing elements on the waste products. The enrichment on fine particles is important in higher atmospheric mobilities and greater potential toxicity [1]. Enrichment factor is convenient to assess the enrichment on fly ash and stack concentrations of a trace element relative to that in coal, without considering variability of characteristics such as moisture and ash content in coals. The enrichment factors are generally normalized to the concentration of an element which is assumed to be non-volatile under combustion conditions. The element Al is often used and the enrichment factor (EF) of an element is related to the concentrations (C) of Al in coal as follows:

$$EF = \frac{C_{element\ output} \times Q_{element\ output}}{C_{Al\ output} \times Q_{Al\ output}}$$

$$= \frac{C_{element\ coal} \times Q_{coal\ input} + C_{element\ sorbent} \times Q_{sorbent\ input}}{C_{Al\ coal} \times Q_{coal\ input} + C_{Al\ sorbent} \times Q_{sorbent\ input}}$$

$$C_{ij} : \text{Concentration of element of } i \text{ in stream of } j \ [mg/\text{kg}]$$

$$Q_{ij} : \text{Mass flowrate } [kg/h]$$

When the EF is more than one, it means that the trace element is condensed. Figures 5(a), and 5(b) are figured from Figures 3(a) and 3(b) by above definition.
of the EF. Non-volatile elements of group-1 as shown in Figure 5(a), essentially, should show the same behavior as Al but Ca, Mn, Co, and Cr have deviations. Plant-4 using Mg(OH)$_2$ as sorbent to reduce SOx gives a large deviation because of low mass balance in Fig.2. On the other hand, the enrichment factors of volatile elements of group-4 show less than one, near 0.1, suggesting such elements are vaporized at the combustor. Group-2 and 3 are dependent on the plant with different flue gas temperature and flue gas control equipments.

The behaviors of group-1, 2 and 3 in fly ash as shown in Figure 5(b) are basically similar to in bottom ash. Different is semi-volatile and volatile elements of group-3, 4 and 5, which are enriched on fly ashes. The trend is to increase with volatility of elements. However, the enrichment factors are around one and which are lower than previous data reported [1, 3].

It would be very difficult from these enrichment factors obtained here that we conclude some influence of combustion conditions and flue gas control equipments.

Figs. 5(a) and 5(b): Enrichment factors of elements in bottom ash (a) and in fly ash (b)
4 Discussion

4.1 Effects of mass balance on enrichment factors

To clear why enrichment factors of fly ashes were almost one for any plant, we estimated the effect of mass balance and the responsibility on the factors. If the destination and the fraction of ash are different, enrichment factor referring Al should be changed. Assuming that the Al in the bottom ash and in the fly ash is respectively 27% and 73%, increase of the percentage of bottom ash against fly ash should decrease the enrichment factors for the bottom and increases it for the fly ash. Even though the percentage changes a range of 0% to 60%, however, the order of magnitude can be unchanged, suggesting that influence of the errors of mass balance including Al should be low. On the other hand, the effect of concentration of trace element is also ineffective on the calculation of this enrichment factor comparing with Al described above. It is still that there is some controversy as to the validity of data by complex sampling and analytical techniques.

4.2 Removal efficiency of each flue gas control

Flue gas control such as EP, bughouse and cyclone showed high efficiencies for non-volatile elements, more than 90%, especially baghouse was the highest in this work. However, efficiencies for volatile elements such as Hg and Br gave wide distribution and depend on the flue gas control system. Additional FGD control is available further to capture non-volatile and some of volatile elements. However, the removal efficiency for volatile elements of Group-4 and 5, such as Hg, is widely distributed, which indicates to be dependent on the system and/or the type of FGD.

4.3 Enrichment factor in dust at stack

Enrichment factors in bottom ash and fly ash were shown in Figure 5(a), and 5(b). However, as shown in Figure 3(c), Al in particulate dust recovered at stack was too low to estimate the enrichment factor for the stack gas. Therefore, based on the proper mean flow rate and concentration of particulates in flue gas, also assuming that all of elements in stack gas are adsorbed on a little of fine particulate dust, we could estimate the enrichment factors for several plants. The results are shown in Figure 6. It suggests that the enrichment factors are increased with volatility of elements. Group-1 has a range between 1 and 100, Group-2 and 3 are between 10 and 1000, and Group-4 and 5 between 100 and 10000 behavior, which is significantly higher than those for bottom ash and fly ash within 10 at maximum. This means that volatile elements easily condense in or on fine particulates.
4.4 Concentration of each element at stack gas

Removal efficiency of toxic elements such as Pb, Cd, As, Se and Hg by dust collector is dependent on the system of the plant and at least Se, Hg and halogen elements are not completely removed. These would be emitted from stack to the air. The concentrations are shown in Table 2.

Table 2: Concentrations of elements at stack.

<table>
<thead>
<tr>
<th></th>
<th>Plant-1 mg/m³N</th>
<th>Plant-2 mg/m³N</th>
<th>Plant-3 mg/m³N</th>
<th>Plant-4 mg/m³N</th>
<th>Plant-5 mg/m³N</th>
<th>Plant-6 mg/m³N</th>
<th>Plant-7 mg/m³N</th>
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<tbody>
<tr>
<td>Al</td>
<td>0.300</td>
<td>12.00</td>
<td>0.009</td>
<td>19.47</td>
<td>10.71</td>
<td>0.0347</td>
<td>0.0810</td>
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<tr>
<td>Si</td>
<td>0.250</td>
<td>0.590</td>
<td>0.002</td>
<td>278.5</td>
<td>9.198</td>
<td>0.0205</td>
<td>0.0550</td>
</tr>
<tr>
<td>Ca</td>
<td>0.091</td>
<td>0.550</td>
<td>0.033</td>
<td>10.21</td>
<td>0.809</td>
<td>0.0123</td>
<td>0.1930</td>
</tr>
<tr>
<td>Mg</td>
<td>0.016</td>
<td>0.160</td>
<td>0.225</td>
<td>4.841</td>
<td>1.617</td>
<td>0.0077</td>
<td>0.0035</td>
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<tr>
<td>Mn</td>
<td>0.340</td>
<td>0.065</td>
<td>0.002</td>
<td>0.3580</td>
<td>0.450</td>
<td>0.0014</td>
<td>0.0008</td>
</tr>
<tr>
<td>Co</td>
<td>0.006</td>
<td>0.003</td>
<td>0.002</td>
<td>0.0947</td>
<td>0.046</td>
<td>0.0014</td>
<td>0.0013</td>
</tr>
<tr>
<td>Cr</td>
<td>0.030</td>
<td>0.034</td>
<td>0.002</td>
<td>0.0947</td>
<td>0.215</td>
<td>0.0026</td>
<td>0.0008</td>
</tr>
<tr>
<td>Fe</td>
<td>0.170</td>
<td>1.000</td>
<td>0.006</td>
<td>26.62</td>
<td>3.234</td>
<td>0.0280</td>
<td>0.0100</td>
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<tr>
<td>Cu</td>
<td>0.200</td>
<td>0.032</td>
<td>0.002</td>
<td>0.1473</td>
<td>0.440</td>
<td>0.0014</td>
<td>0.0008</td>
</tr>
<tr>
<td>P</td>
<td>2.000</td>
<td>2.000</td>
<td>0.002</td>
<td>0.0611</td>
<td>1.770</td>
<td>0.0014</td>
<td>0.0240</td>
</tr>
<tr>
<td>Ni</td>
<td>0.063</td>
<td>0.010</td>
<td>0.002</td>
<td>0.1473</td>
<td>0.137</td>
<td>0.0014</td>
<td>0.0013</td>
</tr>
<tr>
<td>Be</td>
<td>0.004</td>
<td>0.004</td>
<td>0.002</td>
<td>0.0104</td>
<td>0.014</td>
<td>0.0014</td>
<td>0.0008</td>
</tr>
<tr>
<td>Zn</td>
<td>0.081</td>
<td>0.036</td>
<td>0.002</td>
<td>0.3790</td>
<td>1.099</td>
<td>0.0267</td>
<td>0.0008</td>
</tr>
<tr>
<td>Pb</td>
<td>0.450</td>
<td>0.220</td>
<td>0.002</td>
<td>0.1457</td>
<td>0.207</td>
<td>0.0020</td>
<td>0.0008</td>
</tr>
<tr>
<td>Cd</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>0.0065</td>
<td>0.0006</td>
<td>0.0014</td>
<td>0.0008</td>
</tr>
<tr>
<td>Sn</td>
<td>0.170</td>
<td>0.075</td>
<td>0.002</td>
<td>0.0104</td>
<td>0.100</td>
<td>0.0020</td>
<td>0.0008</td>
</tr>
<tr>
<td>V</td>
<td>0.010</td>
<td>0.010</td>
<td>0.002</td>
<td>0.4630</td>
<td>0.154</td>
<td>0.0014</td>
<td>0.0008</td>
</tr>
</tbody>
</table>
The concentrations of the stack gases are considerably low even when comparing with the value of the regulation of foreign country. However, without wet FGD, concentration would be several times to several tens times increased. Installation of FGD is very available to remove the trace elements in flue gases from stack.

5 Conclusions

Although the number of data is restricted, we investigated effects of boiler type, flue gas treatment apparatus on the fate of trace elements in combustion process. As results, we can conclude

1) As particulate control apparatus, fabric filter is more available to capture particulates with trace elements than the electrostatic precipitator.
2) Capturing volatile elements such as Hg, Br and F by fly ash of pulverized coal combustion is ineffective and capturing by FBC is considerably available.
3) Removal efficiency and enrichment factor by bottom ash at boiler are dependent on the combustion temperature.
4) Removal efficiency and enrichment factor by fly ash at flue gas control are strongly dependent on the operating or sampling temperature.
5) Enrichment factors in bottom ash and in fly ash are gradually decreased with volatility of element, although which is nearly one.
6) Enrichment factors in stack gas are extraordinarily increased with volatility of elements.
7) Any concentration is below the regulation value of foreign countries.

This study suggests condensation of trace elements in fine particle or particulates, especially, volatile elements as Se and Hg.

References