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4. Conclusions

The exhaust gas with hydrocarbons generated from pyrolysis process was treated by using the ceramic filter at 570 K. The pressure loss caused by adhered hydrocarbons was measured, and the regeneration methods of pulse jet and thermal treatment were evaluated. The following facts were obtained.

- (1) The oil mass adhered on unit surface area of the ceramic filter increases with the filtration time. The pressure loss in filter is proportional to the square of adhered oil mass. The obtained experimental equation is similar to that for the collection of solid particles.
- (2) For the dislodgement for adhered hydrocarbons, the thermal treatment above 720-780 K for 7200 s is valid, but the pulse jet method is not.
- (3) For the thermal treatment, the temperature higher than boiling point of hydrocarbons is required.

Nomenclature

| | |
|---|----------------------|
| D : depth of planar ceramic filter | (m) |
| ID : inside diameter of cylindrical ceramic filter | (m) |
| L : length of cylindrical ceramic filter | (m) |
| M_p : cumulative fed polystyrene mass per unit surface area of filter | (kg/m ²) |
| m_h : adhesive oil mass on unit surface area of filter | (kg/m ²) |
| OD : outside diameter of cylindrical ceramic filter | (m) |
| R_r : regeneration ratio | (-) |
| t : time | (s) |
| t_T : thermal treatment time | (s) |
| t_f : filtration time | (s) |
| W : width of planar ceramic filter | (m) |
| W_{hc} : weight of product hydrocarbon | (g/g-sample) |
| u : filtration velocity | (m/s) |
| ΔP_f : total pressure loss in filter | (Pa) |

subscripts

0 : unloaded, 1 : after dislodgement, 2 : before dislodgement

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RELATIONSHIP BETWEEN CHLORINE AND TRACE ELEMENTS IN COAL COMBUSTION PROCESS

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ABSTRACT

Based on the measurement data in industrial coal combustion boilers, the relationship between Cl in coal and the removal behavior of the volatile trace elements (Hg, Se, As) was studied. It was found that an enrichment factor of trace elements in fly ash is increased, and that the output ratios of trace elements in gas phase from stack are decreased when the Cl concentration in coal is increased. Effects of Cl on Hg emission were strongest among the elements studied. Additionally, the difference of emissions of these elements was also discussed when flue gas control equipment or boiler type is different.

KEYWORDS

Coal Combustion, Chlorine, Trace Elements

INTRODUCTION

Most elements in periodic table are contained in coal. When coals are burnt, pollutants such as SO_x, NO_x, particulates and toxic metals are discharged as gas phase from combustion processes. The flue gas treatment systems of fly ash collector, flue gas desulfurization, and selective catalytic reduction of NO_x are available to control the pollutants as SO_x, NO_x and particulates under the present regulations. However it has not been confirmed that its systems can control the toxic metals. If coal consumption would be significantly increased, although concentration of trace elements in coal is very low, effects of trace elements and the local environment would be concerned ¹⁾.

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In order to understand the fate of the trace elements in conventional coal combustion processes, some investigations have been carried out ^{2,3}. However, information of emission behavior of trace elements in commercial plants is very few. Fortunately, the environmental committee of Japan Environmental Management Association for Industry was studied the behaviors of 23 elements (Al, As, Br, Be, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, Mg, Mn, Ni, P, Pb, Se, Si, Sn, V, Zn) from ten industrial coal combustion boilers and effectiveness of conventional flue gas control equipments to investigate the trace element emissions from stack ⁴.

In this study, the relationship between Cl in coal and emission of trace elements in ten coal combustion processes was discussed. Cl in coal can combine with almost trace elements and form chloride in the temperature range of combustion zone and cooled flue gas. Therefore it is thought that Cl is related strongly with the removal of trace element by adsorption of chloride by fly ash or dissolved by a wet flue gas desulfurization. It is important for elucidation of formation mechanisms to clear the behavior of trace elements in commercial plants.

Especially, we pay attention to behavior of volatile elements of Hg, Se and As. Although these semi-volatile or low volatile elements are almost collected by conventional flue gas control equipments, the volatile elements are emitted into the atmosphere ⁴. From an atmosphere environmental point of view, the formation mechanisms and the emission control of the trace elements would be relatively more strongly concerned.

COAL COMBUSTION PROCESSES

A typical temperature distribution of pulverized coal combustion process is shown in Fig. 1. When coal is burnt in a boiler, a part of trace elements in coal go to the bottom ash. But most of trace elements are moved to downstream of the furnace with flue gas. In post combustion zone, the trace elements are collected by particulate control devices such as electrostatic precipitators (EP) or fabric filter (bag filter), and also removed in a wet FGD.

Detailed information of the ten plants that investigated in this study is shown in Table 1. Seven plants are pulverized coal combustion processes (PC). Others are bubbling and circulating fluidized bed boiler processes (FBC). Flue gas cleaning equipments are: electrostatic precipitators (EP) and fabric filters (Bughouse) as particulate control. Four PC plants have wet de-SO_x scrubbers as flue gas desulfurization (FGD). Selective catalytic reduction (SCR) is employed in three PC plants as NO_x control.

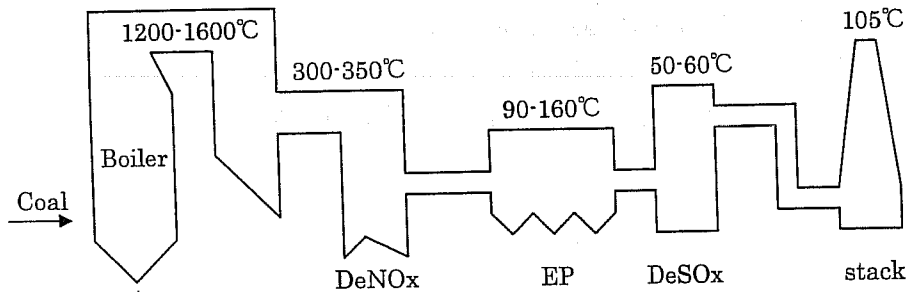


Fig.1 A typical process of pulverized coal combustion processes

Table 1 Type of boiler and flue gas equipment measured [4]

| Plant | Boiler type | Scale* | Ash corector | De-NOx | De-SOx | Cl in coal, ppm |
|----------|-----------------|--------|--------------|--------|------------------------|-----------------|
| Plant 1 | Bubbling FBC | Small | Bag house | Non | In bed | 83 |
| Plant 2 | PC | Middle | EP | Non | Non | 72 |
| Plant 3 | PC | Large | EP | SCR | Mg/Ca(OH) ₂ | 250 |
| Plant 4 | PC | Small | EP | Non | Mg(OH) ₂ | — |
| Plant 5 | PC | Large | EP | SCR | Mg(OH) ₂ | — |
| Plant 6 | PC | Middle | Bag house | Non | Non | 350 |
| Plant 7 | Circulating FBC | Small | Bag house | Non | In bed | 356 |
| Plant 8A | Circulating FBC | Small | Bag house | Non | In bed | 21 |
| Plant 8B | Circulating FBC | Small | Bag house | Non | In bed | 170 |
| Plant 9 | PC | Large | EP | SCR | Mg(OH) ₂ | 200 |
| Plant 10 | PC | Small | EP | Non | Non | 38 |

*: Small, Middle and Large are respectively about 10 to 20 t/h, 20 to 30t/h and more than 30 to 60 t/h of coal feed rate.

EFFECTS OF CHLORINE ON BEHAVIOR OF TRACE ELEMENTS

Cl in coal is devolatilized during combustion, and it combine with almost trace elements. In removal behavior of trace elements, it is important to concern formation of chlorine compounds.

The difference in the concentration of Cl in coals is in wide range from 21 ppm to 356 ppm as shown in Table 1. Effects of the concentration of Cl in coal on the removal behavior of the trace elements were investigated from results of ten plants.

Relationship between Cl concentration in coal and enrichment factors of trace elements

The enrichment factor (EF) is defined as follows ⁴⁾. Here we use Al as a standard element that is assumed to be non-volatile under combustion conditions.

$$EF = \frac{\frac{C_{element\ output} \times Q_{output}}{C_{Al\ output} \times Q_{output}}}{\frac{C_{element\ coal} \times Q_{coal\ input} + C_{element\ sorbent} \times Q_{sorbent\ input}}{C_{Al\ coal} \times Q_{coal\ input} + C_{Al\ sorbent} \times Q_{sorbent\ input}}} \quad (1)$$

C_{ij} : Concentration of element of i in stream of j (mg/kg)

Q_{ij} : Mass flow rate (kg/h)

Fig.2 shows the relationship between Cl concentrations in coal and trace elements enrichment factors. The trend is showed that the trace elements enrichment factors for fly ash increases with the increase of Cl concentration in coal. A positive relationship is found for the three trace elements. But the concentrations of Cl and the trace elements in coal show almost no relationships. Even the relationship between Cl concentrations in coal and trace elements enrichment factors for bottom ash are not also showed. Therefore, it is thought that Cl and trace elements form chlorides like equilibrium prediction at low temperature, and then the chlorides are physically and/or chemically absorbed by fly ash (even the mechanism has not been well recognized), or the chloride such as $HgCl_2$ condense on the fly ash particles because of less volatility of $HgCl_2$.

In Fig.2, the effect of Cl on Hg is the strongest among the three trace elements. When Cl concentration in coal increase from 38ppm to 365ppm, the enrichment factors of Hg, Se and As for fly ash increase to 11.6, 2.9 and 2.5 times, respectively. A similar trend is obtained for other elements (Cd, Pb, Ca, Mn, Ni, Cu, Fe), but the effect of Cl on these elements is small. The enrichment factors of these elements was 1.1~1.5 time.

It is likely that Hg has advantage in the reaction with Cl because of the volatility of Hg which almost exists in gas phase.

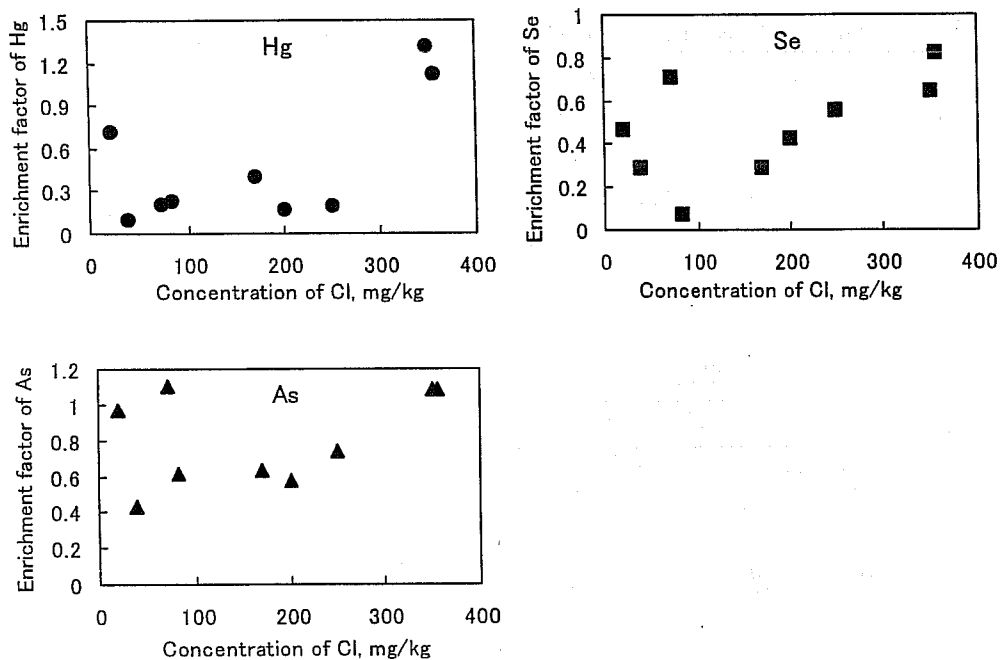


Fig.2 Relationship between Cl concentration in coal and enrichment factors of Hg, Se and As in fly ash

Relationship between Cl concentration in coal and emissions of trace elements

The relationship between Cl concentrations in coal and output ratios of trace elements at stack is shown in Fig.3. Results for four different plants are indicated. It appears that the output ratios decrease with increasing Cl concentration although the combustion process of each plant differs. The output ratio of Hg is higher than that of Se and As. It is found that Cl in coal can affect strongly the emissions of Hg.

The average removal efficiencies of the trace elements in fly ash for pulverized coal combustion processes are shown in Fig.4. The removal efficiency of a fabric filter (Bag) is higher than that of electrostatic precipitator (EP). Especially, the average removal efficiency of Hg in electrostatic precipitators (Plant 2, 3, 9, and 10) is only 22%, but it is more than 92% in plant6 that has a fabric filter. An electrostatic precipitator collects almost all particles. On the other hand, a fabric filter can grasp some gaseous compounds including chlorides, and it can also collect 0.01 μ m particulates that enriched

trace elements ⁴⁾. Therefore, removal efficiency in a fabric filter is higher than that of EP.

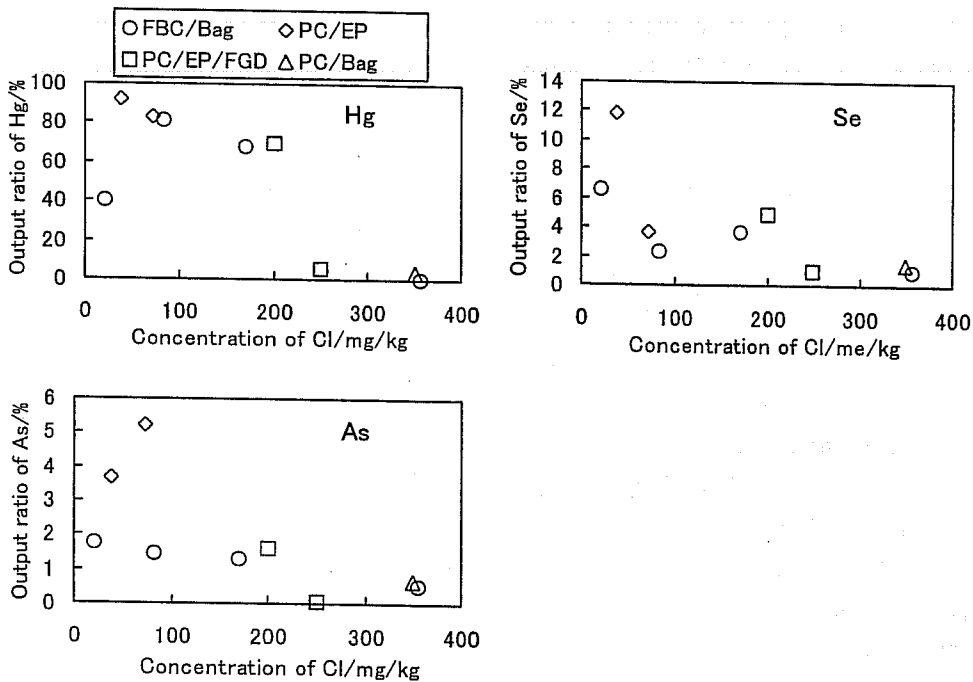


Fig.3 Relationship between Cl concentration in coal and output ratio of Hg, Se and As in fly ash

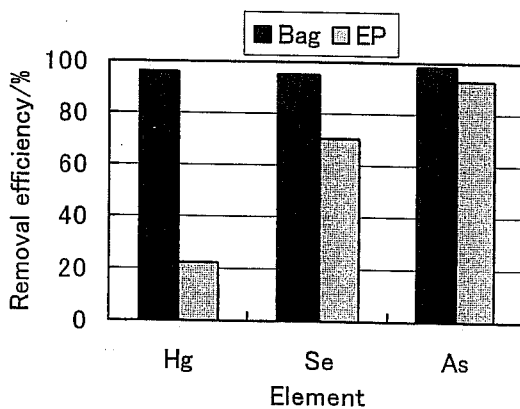


Fig.4 Average removal efficiencies of Hg, Se and As in fly ash for pulverized coal combustion process

Difference in output ratios of the trace elements at stack for different combustion systems are shown in Fig.5. Plant 6 is a pulverized coal fired boiler, and plant 7 is a circulating fluidized bed boiler as listed in Table 1. CFBC (Plant 7) system shows lower output ratios than PC (plant 6) for any trace elements because of the presence of fabric filter and the high Cl concentration in coal. It should also be added that the increase of unburned carbon in CFBC was increased capture ratio of Hg by adsorption on the carbon surface.

The average output ratios of the trace elements at stack for tow plants with and without a wet FGD are compared in Fig.5. Plant 3 and plant 9 is PC boiler with a wet FGD, and Plant 2 and Plant 6 is PC boiler without a wet FGD. Average Cl concentration of coal used in these boilers are 211 ppm and 225 ppm, respectively. In this case, effects of Cl on output ratios can be ignored.

The average output ratios of PC plants with a wet FGD are lower than other plants without a wet FGD. Even Plant 6 (without a wet FGD) having fabric filter equipment, the removal efficiency is much higher than Plant 3 having wet FGD system and electrostatic precipitator. The dissoluble elements are also removed effectively in a wet FGD. It is found that the output ratio of trace elements in plants having a wet FGD system is the lowest in all coal fired systems.

The gaseous oxide, hydride and elementary substance of these trace elements hardly dissolve in water. Therefore, it seems that the decrease of output ratios in a wet FGD is the effect of the water-soluble chloride.

From these results, it is found that use of high Cl coals in PC plants with a wet FGD is available to reduce volatile elements emission.

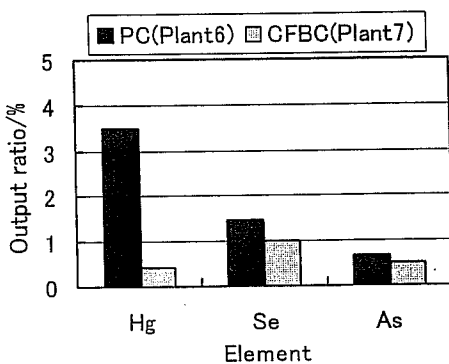


Fig.5 Output ratios of Hg, Se and As at stack for different boilers

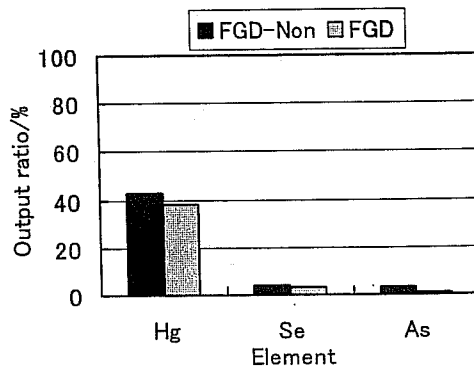


Fig.6 Output ratios of Hg, Se and As at stack with/without FGD.

CONCLUSIONS

- 1) The relationship between Cl in coal and the removal behavior of the volatile trace elements (Hg, Se, As) in coal combustion processes were investigated. It is found that the trace element enrichment factors of fly ash are increased with increasing Cl concentration. Therefore, the output ratios of trace elements at stack are decreased in high Cl coal.
- 2) Effects of Cl in coal on Hg emission were strongest among the studied elements, although similar trend was obtained for these elements.
- 3) Fabric filter facilities can capture volatile trace elements than electrostatic precipitator. However, the reduction efficiency of trace element emission depends on FGD system than particulate control devices.
- 4) The average output ratios of PC plants with a wet FGD are lower than other plants without a wet FGD. It seems that the dissoluble elements are removed effectively in a wet FGD.

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