



Measurements of mercury speciation and fine particle size distribution on combustion of China coal seams

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HIGHLIGHTS

- Quantified effect of Hg and Cl concentration on mercury speciation in flue gas.
- Isokinetic model with multiple linear regression and iterative methods.
- Evaluation of effect of mineral composition of coal on fine particle formation.

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ABSTRACT

The percentage of mercury that is removed in currently used air pollution control devices (APCDs) depends on the speciation in the flue gas exhausting from the coal combustor. Bench-scale measurements were carried out in the flue gas from combustion of different types of coal in a drop-tube furnace set-up to better understand the formation process of three mercury species, i.e. Hg^0 , Hg^{2+} and Hg_p , in gaseous phase and fine particles. It was observed that due to chemical reaction kinetics limitations, higher mercury concentrations in flue gas lead to lower Hg^{2+} proportions. The concentration of chlorine has the opposite effect, not as significantly as that of mercury though. With the chlorine concentration increasing, the proportion of Hg^{2+} increases. Combusting finer sized coal powders results in the formation of more Hg^{2+} . Mineral composition of coal and feed coal particle size has a great impact on fine particle formation. Increased Al in coal results in more finer particle formation, while Fe in coal increases concentration of larger particles. The coexistence of Al and Si can enhance the particle coagulation process. This process is also enhanced at higher coal feed rates, and when feed coal particle sizes are smaller. Results from oxy-coal and conventional air combustion were compared.

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1. Introduction

Coal combustors for electricity production are one of the largest sources of global anthropogenic mercury emissions [1]. Mercury is initially released from the coal in the elemental form. The mercury speciation during coal combustion consists of two processes, homogeneous mercury oxidation in the gaseous phase and heterogeneous mercury adsorption onto the particles. A large fraction of the mercury remains in the gaseous phase [2–10]. Electrostatic precipitators (ESPs) can remove over 99% of the particulate mercury (Hg_p), and wet flue gas desulfurization (WFGD) systems, if present, can retain 67–98% of the gaseous oxidized mercury (Hg^{2+}) [10]. It is therefore important to understand the mercury

oxidation mechanisms in the flue gas. Chlorine related species are known to be important oxidizing agents for mercury [11]. Other flue gas constituents such as SO_2 , NO, H_2O ; are reported to have secondary effects on the rate of the mercury oxidation [12,13].

To determine the mercury oxidation mechanism, kinetic and thermodynamic data were either calculated or obtained from simplified chamber experiments [12–15]. The assumption of gas-phase equilibrium for the mercury oxidation process in exhaust gases from coal combustors is not valid at temperatures below approximately 800 K [11]. The reaction mechanism begins with the kinetic framework proposed by Widmer et al. [16]. In the flue gas, conversion of HCl to Cl_2 is kinetically limited. At temperatures similar to those in the inlet to the APCD, equilibrium estimations indicate that half of the chlorine will be in the form of Cl_2 , but kinetic calculations show that less than 1% of the chlorine is converted to Cl_2 [11]. The oxidizers such as Cl, Cl_2 and HOCl are all generated from HCl.

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The above conclusions above were drawn primarily from experiments conducted in a simulated gas chamber system. However, the coal combustion process is much more complicated, with several reactions taking place simultaneously. Bench-scale measurements on mercury speciation and fine particle formation in a coal combustor were performed in this study to obtain a more comprehensive understanding of the mercury speciation mechanism under more realistic scenarios. Different types of Chinese coal samples with diversity in rank, mercury content, chlorine and ash content were combusted in a drop-tube furnace system. The variation of these characteristics allowed to study the impact of parameters such as coal type, coal particle size and combustion condition on the fine particle formation and mercury speciation.

2.1. Set-up and analysis

The major parts of the experimental system, shown in Fig. 1, are: the coal feeder, drop-tube furnace, exhaust flue gas line, scanning mobility particle sizer (SMPS) and the mercury sampling train. A filtered air compressor provided dry air for the conventional air-coal combustion, and a mixture of CO₂ and O₂, supplied from gas cylinders, were used for the oxy-coal condition. Prior to entry of gases into the drop tube furnace, the flow passed through a fluidized-bed coal feeder to carry a certain amount of coal to the furnace. The drop tube furnace (Lindberg Blue M, ThermoElectron Co.), containing an alumina reactor tube with an inner diameter of 2.25 in. and a length of 4 feet, was equipped with a temperature

The flue gas was sampled through a mercury speciation sampling train before the impactor. Particulate mercury was captured by a glass fiber filter, while gaseous mercury (Hg^0 and Hg^{2+}) was absorbed by flowing through a set of impingers. A 2.5 lpm flow of flue gas was bubbled through the impingers for 3–4 h. Iodine Based Method developed by Hedrick et al. [20] was adopted in this study for gaseous mercury speciation measurement. The first two impingers were equipped with 15 ml of 1.0 M tris-EDTA buffer solution for the capture of Hg^{2+} , followed by one impinger with 15 ml solution of 10% hydrogen peroxide (H_2O_2) and 2% nitric acid (HNO_3) for removing reductive gas, e.g. SO_2 , and two impingers with 15 ml of 0.05 M potassium iodide (KI) and 2% hydrochloric acid (HCl) for the capture of Hg^0 . Another impinger with silica gel was added to prevent moisture from entering the pump. Particles collected on the glass fiber filter were analyzed by a direct mercury analyzer (DMA80, Milestone) for Hg_p . The impinger solutions were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500CE).

Real-time sub-micrometer particle size analysis was performed downstream of the impactor by a scanning mobility particle sizer (SMPS, TSI Inc.) to obtain the particle size distribution in the range of 9–425 nm. The sub-micrometer fly ash particles collected on the glass microfiber filter were photographed by a scanning electron microscope (SEM, Hitachi S4500) to determine the particle morphology.

Proximate and ultimate analyses, together with mercury and chlorine content analysis, were conducted for all the coal samples

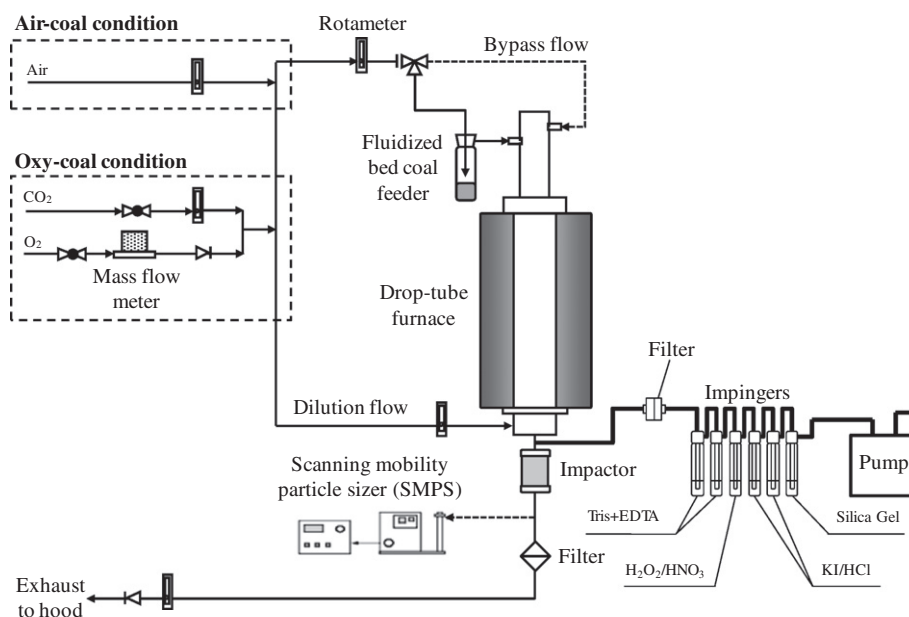


Fig. 1. Drop-tube furnace system used combustion of coal seams.

used in the experiment. All the analytical methods for coal adopted in this study can be found in the [supporting information](#) (Table S1). The XRD analysis of metal–oxide content was performed using a Rigaku Geigerflex D-MAX/A diffractometer, the MDI mineral database, and Jade Plus software.

2.2. Test plan

Three sets of tests were conducted in this study. The objective of the first set of experiments (Set I) is to compare the calculated and observed value of oxidized mercury. The second set of experiments (Set II) was performed to determine the effect of calorific value of coal, coal particle size and the combustion condition (conventional or oxy-combustion) on mercury speciation. The third set of experiments (Set III) was to establish the effect of coal feed rate, coal particle size and combustion condition on particle size distribution in the exhaust. The overall test plan is summarized in [Table S2](#) in the [supporting information](#).

2.3. Coal characterization

Five types of Chinese coal samples (labeled S01, S04, S07, S09, S10) of various ASTM ranks were selected for this study. The coal analysis results and coal ranks were listed in [Table 1](#). The Powder River Basin (PRB) sub-bituminous coal was also used for comparison. The mercury content of coal varied largely from 20 to 673 µg/kg, while the chlorine content of coal significantly within the range of 120 to 3610 mg/kg. Compared with the Chinese coal, the PRB coal had lower mercury and chlorine content, higher fixed carbon content, lower ash content and higher heating value.

The mineral composition of four Chinese coal samples with different ranks obtained from XRD analysis was shown in [Fig. S1](#) in the [supporting information](#). Kaolinite was the dominant mineral in S01 coal. S04 was dominated by kaolinite and pyrite, with considerable amounts of quartz and calcite. Boehmite, kaolinite and a certain amount of calcite were the main mineral contents of S07. S10 was mainly quartz. The main mineral elements of S01 were Al and Si; those of S04 were Al, Si and Fe; that of S07 was Al; and that of S10 was Si.

3. Results and discussion

3.1. Effect of Hg and Cl concentration on mercury speciation in flue gas

When actual coal samples are combusted, independent control of chlorine and mercury concentrations is not possible. Therefore, the effect of chlorine and Hg concentration were evaluated simultaneously. Multiple linear regression (MLR) and iterative methods were used in this study for data analysis. The rate expression for Hg conversion is given by:

$$\frac{dc_{\text{Hg}}}{dt} = -k \cdot c_{\text{Hg}}^{\alpha} \cdot c_{\text{HCl}}^{\beta} \quad (1)$$

where c_{Hg} is the gas phase elemental Hg concentration; c_{HCl} is the gas phase HCl concentration; k is the overall reaction rate constant;

and α and β are the reaction orders with respect to the concentrations of Hg and HCl, respectively. On integrating Eq. (1), the following is obtained:

$$c_{\text{Hg}}^{1-\alpha} - c_{\text{Hg},0}^{1-\alpha} = (\alpha - 1) \cdot k \cdot t \cdot c_{\text{HCl}}^{\beta} \quad (2)$$

where $c_{\text{Hg},0}$ is the original gas phase elemental Hg concentration, i.e. total gaseous Hg.

By multiplying by $c_{\text{Hg},0}^{\alpha-1}$ on both sides and alternating $1 - c_{\text{Hg}}/c_{\text{Hg},0}$ with P_o which is the percentage of oxidized mercury in total gaseous mercury:

$$1 - (1 - P_o)^{1-\alpha} = (1 - \alpha) \cdot k \cdot t \cdot c_{\text{HCl}}^{\beta} \cdot c_{\text{Hg},0}^{\alpha-1} \quad (3)$$

By taking the natural log on both sides:

$$\ln[1 - (1 - P_o)^{1-\alpha}] = \ln[(1 - \alpha) \cdot k \cdot t] - (1 - \alpha) \ln c_{\text{Hg},0} + \beta \ln c_{\text{HCl}} \quad (4)$$

Based on the measured values of P_o , $c_{\text{Hg},0}$ and c_{HCl} obtained from eight trials of the experiment, a multiple linear regression (MLR) analysis was done using Eq. (4). The initial value for α was assumed to be 0.5. The new value of α calculated by the first iteration was substituted to the left side of Eq. (4) to obtain the next iteration, and this process was repeated. The converged value obtained was:

$$\alpha = 0.381 \quad (5)$$

and,

$$\beta = 0.181 \quad (6)$$

With the estimated converged values of α and β , P_o for each trial was calculated. [Fig. 2](#) shows the comparison between the calculated values and the observed values. The correlation coefficient was 0.94, indicating good agreement of the results.

The effect of mercury and chlorine concentration in the flue gas on the gaseous phase mercury speciation is demonstrated as an isoline diagram in [Fig. 3](#). With increasing concentration of chlorine in the coal, the proportion of Hg^{2+} increased. However, the mercury concentration has a more significant impact on the transformation of Hg^0 to Hg^{2+} than that of chlorine. Lower mercury concentration leads to higher proportion of Hg^{2+} . This confirms that the oxidation reaction of mercury was kinetically limited. If the reaction reached thermodynamic equilibrium, P_o should have only depended on the concentration of chlorine, which can be derived from the chemical reactions between Hg^0 , HgCl and HgCl_2 , shown as following equations:

$$[\text{HgCl}_2] = K_2[\text{HgCl}][\text{Cl}] = K_2K_1[\text{Hg}^0][\text{Cl}]^2 \quad (7)$$

$$P_o = \frac{[\text{HgCl}_2]}{[\text{HgCl}_2] + [\text{Hg}^0]} = 1 - \frac{1}{K_2K_1[\text{Cl}]^2 + 1} \quad (8)$$

3.2. Effect of calorific value of coal on mercury speciation in flue gas

The average value of the overall reaction rate coefficient k was used so as to simplify the calculation. However, k reduces

Table 1
Proximate and ultimate analysis results of experimental coals.

Coal name	Proximate analysis				Ultimate analysis					$Q_{\text{net,d}}$ (MJ/kg)	Hg (ppb)	Cl (ppm)	ASTMRank
	M_{ad}	A_{d}	V_{d}	FC_{d}	S_{d}	C_{d}	H_{d}	N_{d}	O_{d}				
S01	8.41	44.64	23.64	31.72	1.47	38.88	2.35	0.64	12.02	13.54	673	120	Lig.
S04	3.80	22.97	10.54	66.49	2.79	67.03	2.55	1.00	3.66	25.98	428	310	Anth.
S07	9.14	24.82	27.80	47.38	0.53	57.69	3.46	0.90	12.60	21.87	202	3610	Subbit.
S09	4.07	30.52	24.27	45.21	0.48	55.72	3.25	0.85	9.18	21.79	35	720	Subbit.
S10	15.71	5.68	34.39	59.93	0.45	74.54	4.39	0.94	14.00	28.48	20	140	Bit.
PRB	27.70	8.00	48.30	42.90	0.57	67.30	4.58	0.96	19.92	28.04	50	100	Subbit.

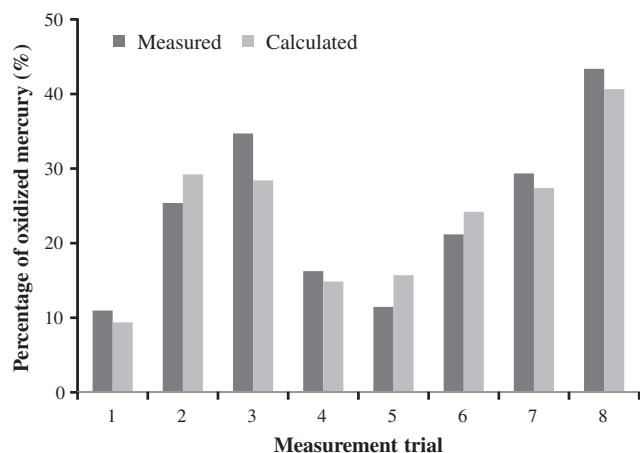


Fig. 2. Comparison of calculated and observed value of oxidized mercury percentage.

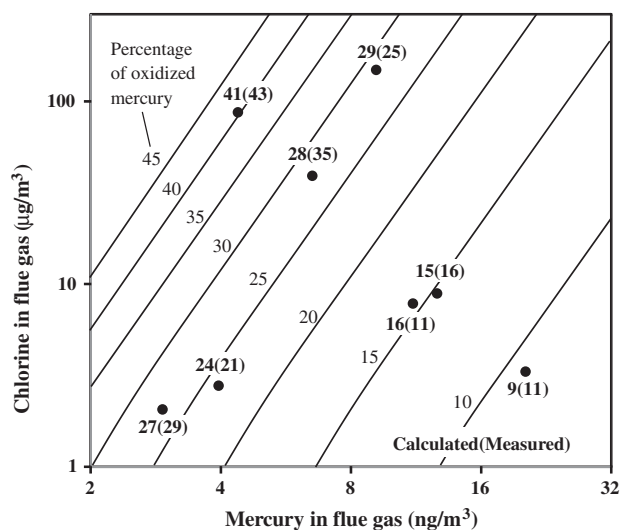


Fig. 3. Effect of mercury and chlorine concentration on percentage of oxidized mercury in flue gas (air-coal condition, 150 mesh in coal particle size). Note: The numbers listed on the curves and besides parentheses are the calculated percentage of oxidized mercury and the numbers in parentheses are the measured percentages of oxidized mercury.

drastically when the flue gas temperature decreases as per the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

where A is a pre-exponential factor; E_a the activation energy; T is the temperature; and R is the gas constant.

As mentioned previously, the mercury oxidation reaction does not proceed if the flue gas temperature is below 800 K. The furnace temperature is 1100 °C, i.e. 1373 K. Therefore, t is the time during which the flue gas temperature decreases from 1373 K to 800 K, and this value is used in Eq. (2). This t could not be measured in this experiment, but t can be considered to be proportional to the heat of combustion which is directly related to the calorific value of coal combusted. Higher calorific value of coal would result in longer time duration for mercury to be oxidized. Therefore, the calorific value of coal could be an important factor for mercury oxidation.

Results from four different types of coal (S01, S04, S07 and S10) were compared to establish the relationship between mercury

speciation and calorific value of coal. High correlation, with a coefficient of 0.99, was found between the proportion of oxidized mercury and the calorific value of coal, indicating that the calorific value of coal could be an important factor. The higher calorific value of the coal results in a longer available time as well as higher temperature, which has been demonstrated to accelerate mercury oxidation.

3.3. Effect of coal particle size on mercury speciation in flue gas

Besides reactant concentration and temperature, coal particle size is one more factor that might have influence on the mercury oxidation. Trials with a constant coal feed rate of the same coal (S04) with different coal particle sizes were conducted to determine the trends. As is shown in Fig. 4a, as the critical coal feed size is changed from 100 μm to 25 μm, the percentage of oxidized mercury in the flue gas gradually increased. Heterogeneous reactions, catalyzed by the active ingredient on the particle surface, play an important role in the mercury oxidation process. Smaller size of coal has a larger total specific surface area, accelerating the catalytic oxidation process. Therefore, finer coal particles enhance the fraction of oxidized mercury. Another reason could be that smaller size of coal results in more complete combustion, and hence results in higher temperature, which accelerates the mercury

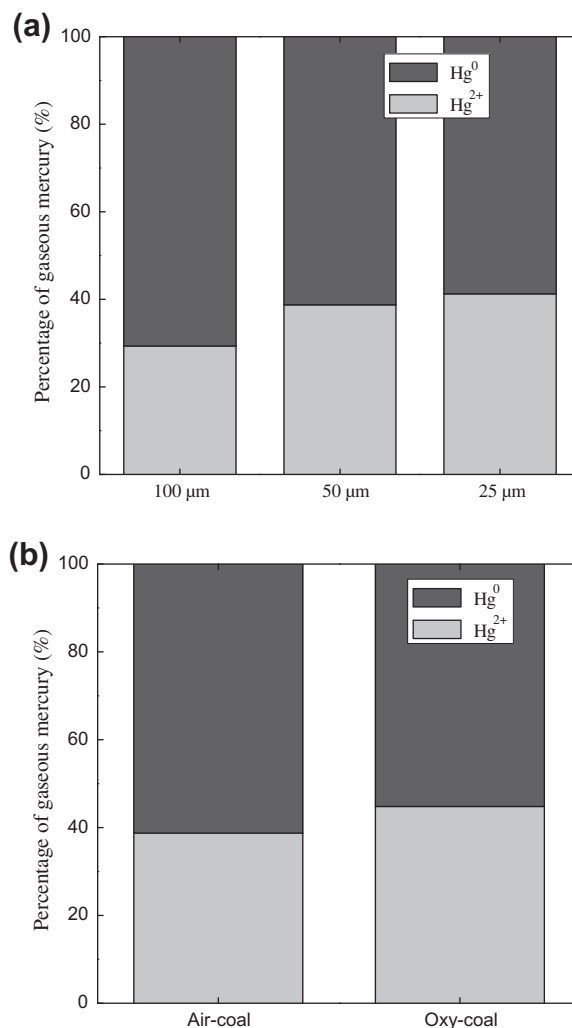


Fig. 4. Mercury speciation in comparison between (a) different coal particle size (S04, air-coal); and (b) air-coal and oxy-coal conditions (S04, 150 mesh). Note: S04 coal was used in these two sets of experiments.

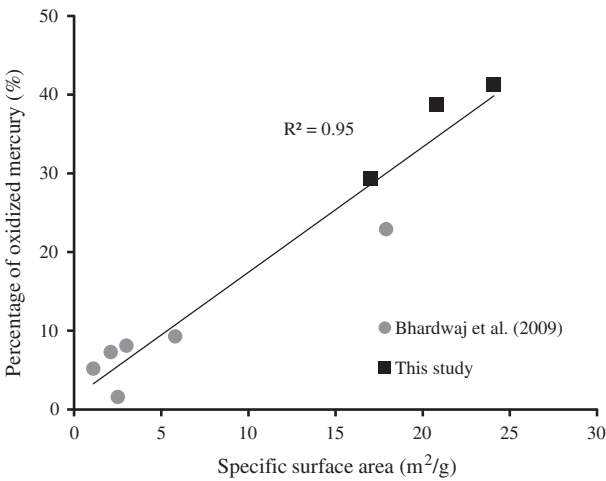


Fig. 5. Relationship between specific surface area and percentage of oxidized mercury.

oxidation process. This is consistent with the discussion in Section 3.2. Based on results from this study and Bhardwaj et al. [17], the relationship between specific surface area and percentage of oxi-

dized mercury was obtained, as shown in Fig. 5. The consistency with the study of Bhardwaj et al. [17] confirmed the effect of coal particle size on mercury speciation.

3.4. Comparing the effect of air–coal and oxy-coal conditions on mercury speciation in flue gas

A mixture of O₂ and CO₂ was used in this study, instead of setting up a recycled flue gas system. Fig. 4b compares the mercury speciation between these two conditions. The coal feed rate and the percentage of oxygen in the gas were the same in both conditions. The oxy-coal condition resulted in a slightly higher mercury oxidation rate than the air–coal condition, but the difference was not significant. Table 2 shows the results from this study and Suriyawong et al. [21]. Suriyawong et al. [21] hypothesized that the oxy-coal condition might not have an effect on mercury speciation. However, theoretically there could be a possible oxidation path for mercury under oxy-coal condition. Metal oxidation is one of the major sub-mechanisms in particle formation. During the metal oxidation process, CO₂ can convert metal to metal oxides [21], and the metal oxides can further convert Hg⁰ into Hg²⁺. Therefore, with the role of metal as a catalyst, CO₂ can act as an oxidizer. The following reactions are the three steps for mercury oxidation:



Table 2
Mercury speciation in air–coal and oxy-coal conditions in different studies.

Condition	This study		Suriyawong et al. [21]		
	Air–coal	20%O ₂ /80%CO ₂	Air–coal	20%O ₂ /80%CO ₂	25%O ₂ /75%CO ₂
Percentage of oxidized mercury (%)	38.7	44.8	20.0	14.3	17.4
Percentage of elemental mercury (%)	61.3	55.2	80.0	85.7	82.6

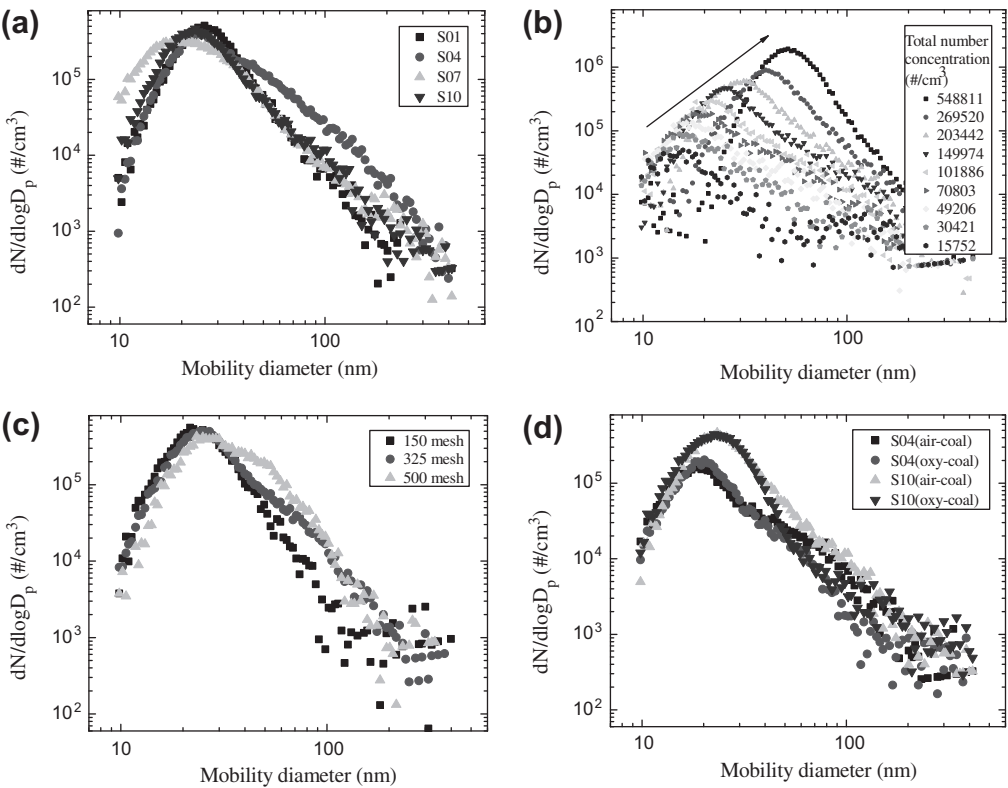
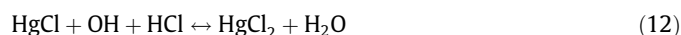
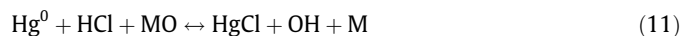
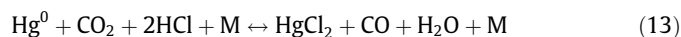


Fig. 6. Particle size distribution in the flue gas resulting from (a) the combustion of different coals (air–coal, 150 mesh); (b) different coal feed rate (S04, air–coal, 150 mesh); (c) different coal powder size (S04, air–coal); and (d) air–coal and oxy-coal conditions.



The total reaction can be summarized as reaction (13):



This effect could be more dominant for the China coal seams, due to the higher ash content in comparison to the PRB coal seams [21].

3.5. Effect of mineral composition of coal on fine particle formation

Mineral composition plays an important part in fine particle formation. There are two paths to form fine particles: one is vaporization and condensation; the other is oxidation and nucleation [21]. For those metals that were more volatile (e.g. Na, Pb, Cd), vaporization and condensation dominate; for those metals or suboxides that were less volatile (e.g. Mg, Al, SiO, Fe), oxidation and nucleation dominate the fine particle formation. Based on the mineral composition of all the samples, oxidation and nucleation tend to be the dominant path.

Fig. 6a shows the fine particle size distribution in the flue gas resulting from the combustion of different coals. S01 and S10 have fewer types of metallic species than S04 and S07, which results in a more uniform particle size distribution. Al and Si are the dominant element in S07 and S10, respectively. The particles generated from the combustion of S07 were finer than those from the combustion of S10, which might due to the smaller size of nuclei generated from Al than from SiO. Larger nuclei would probably shorten the time of nucleation and coagulation. However, the combustion of S01 generated even larger particles than S07 and S10 while it has an equivalent amount of Al and Si as kaolinite. This was probably because Al tends to lose electrons and Si oxide tends to accept electrons, resulting in opposite polarity particles. The coexistence of Al and Si would therefore accelerate the rate of coagulation. The fly ash from S04 had larger particles than the others, which is in accordance with the existence of Fe in S04.

3.6. Effects of feeding rate and particle size of coal on fine particle formation

Higher total fine particle concentrations of fly ash resulted from higher coal feeding rates, which led to larger size particles, as is shown in Fig. 6b. At same coal feeding rates, the smaller size of the inlet coal particles can contribute to the formation of larger fly ash particles (Fig. 6c). The smaller coal particles result in faster combustion rates and subsequent release of metallic species that form a higher concentration of particles. The higher concentration of particles results in faster coagulation rates that result in the formation of larger sized fly ash particles. In the meantime, smaller size of coal would result in more complete combustion, hence results in higher temperature, which could be another reason for this. Further studies are needed to ensure the direct reason.

3.7. Comparing the effect of air-coal and oxy-coal conditions on fine particle formation

S04 and S10 were chosen to be burned under both the air-coal and the oxy-coal conditions. The results of fly ash particle size distribution are summarized in Fig. 6d. No significant difference was found in these two conditions. There were slightly more large particles formed in the oxy-coal conditions, which might be due to the contribution of CO₂ to the metal oxidation process. The metal oxidation process is an important step in fine particle formation [21].

CO₂ can act as a weak oxidizer in both the gaseous mercury oxidation process and the fine particle formation process.

4. Conclusions

To better understand the formation process of the three mercury species, i.e. Hg⁰, Hg²⁺ and Hg_p, bench-scale experiments in a drop tube coal combustion system with measurements in the flue gas were carried out. The focus was on understanding two mechanisms: mercury speciation in the gas phase and fine particle formation. Concentrations of Hg species, residence time in the high temperature regions and particle surface area for catalytic oxidation are important factors for gaseous mercury speciation. The mercury concentration in the coal, and subsequently in the flue gas has the highest impact on the oxidation process. The concentration of chlorine has a similar effect, though not as dominant as the mercury concentration. Systems that result in higher temperatures for longer durations result in greater formation of Hg²⁺. Such conditions are obtained for both higher heating value coal seams, and smaller sized coal feed particles. Mineral composition of coal, coal feeding rate and coal particle size influence fine particle formation. Higher Al in coal seams resulted in greater fine sized particle formation, while larger Fe concentration in coal leads to the formation of larger particles. Al and Si result in opposite polarity particles, and their co-existence in the coal seams results in enhanced coagulation, thus leading to larger particle sizes. The oxy-coal condition results in both enhanced mercury oxidation and metal oxidation in the fine particle formation process. Burning higher chlorine content coal (or adding halogen additives) or finer size coal could be effective approaches for mercury control during coal combustion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2012.06.069>.

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