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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.

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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Larger unburned carbon content (UBC), surface area and particle size of fly ash are reported to increase mercury uptake and oxidation [17]. Tests with single fly ash components indicated that SiO_2, Al_2O_3, MgO, CaO, and TiO_2 had no significant effect on promoting mercury oxidation or adsorption, while Fe_2O_3 may promote mercury oxidation and adsorption [17]. However, the mineralogy, chemical composition, and microstructure of metals (e.g. Fe, Ca, etc.) in fly ash can affect the morphology of the fly ash particles [18,19]. It follows that the morphology of the fly ash particles has considerable impact on the transformation of Hg^0 to Hg^{2+} and Hg_p.

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. Experimental

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 CO_2 and O_2, 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 control device, set to 1100 °C. A flow rate of 3.0 lpm into the furnace was maintained for all the experiments in this study to get a fixed residence time of over 60 s, sufficient to achieve complete char burnout. Particle-free dilution gas was added at the exit of the furnace to quench aerosol dynamics, so that representative aerosol size distribution measurements of conditions at the exit of the furnace were obtained. The ratio of the dilution flow rate to the combustion furnace flow rate was fixed at 1.0 in this study. The diluted exhaust flow first passed through a six-stage cascade impactor (Mark III, Pollution Control System Co.) with a final stage cut-off particle size of 0.5 μm. The remaining fine particles either was sampled by the SMPS or passed through a glass fiber filter to collect all the fine particles for further analysis.

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

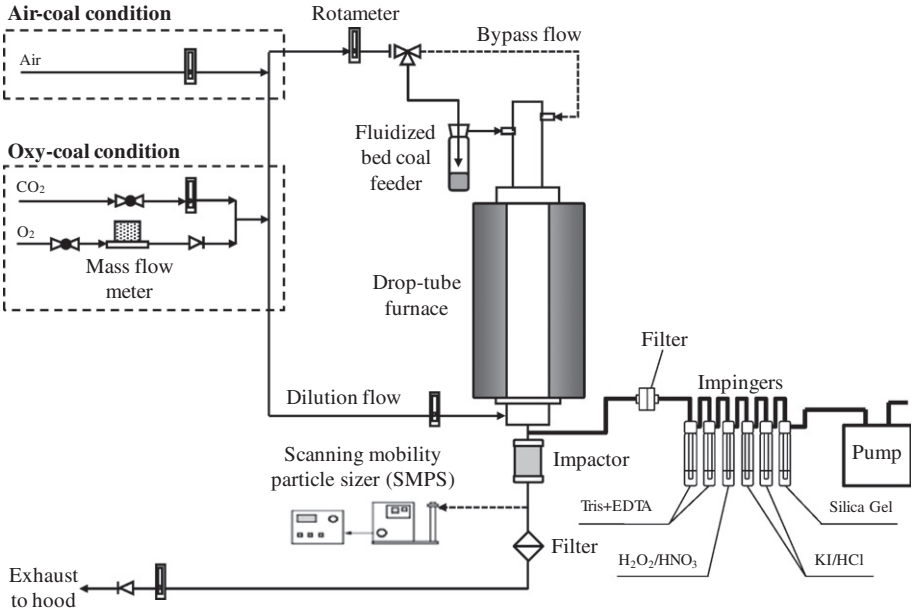

Fig. 1. Drop-tube furnace system used combustion of coal seams.