Submicrometer Particle Formation and Mercury Speciation Under $O_2$–$CO_2$ Coal Combustion

Acharya Suriyawong,†,‡ Michael Gamble,†.§ Myong-Hwa Lee,†,‡ Richard Axelbaum,‡ and Pratim Biswas*†,‡

Aerosol and Air Quality Research Laboratory and Environmental Engineering Science, Campus Box 1180, Washington University in St. Louis, St. Louis, Missouri 63130, and Department of Chemical Engineering, College of Engineering, Architecture, and Technology, Oklahoma State University, Stillwater, Oklahoma 74078

Received April 25, 2006. Revised Manuscript Received September 7, 2006

The characteristics of the submicrometer mode of ash and mercury speciation on combustion of coal in an oxygen–carbon dioxide and air (conventional) system were compared. The experiments were conducted at different $O_2$:$CO_2$ and $O_2$:N$_2$:CO$_2$ mixing ratios. On replacing the nitrogen in air with carbon dioxide, the total mass of the particles in the submicrometer mode (<0.5 μm) of ash was smaller. Correspondingly, the geometric mean size ($d_{50}$) of the submicrometer aerosol was smaller by approximately 28%. When the $O_2$:CO$_2$ ratio was increased from 1:4 to 4:4, the geometric mean size of the submicrometer mode increased from 29 to 54 nm because of a faster vaporization rate as a result of a higher coal particle temperature. An increase in the geometric mean size was observed on increasing the N$_2$:CO$_2$ ratio at a fixed O$_2$ concentration because of the same reasons. The shape of the primary particles was spherical in all the tests, indicating that a vapor to particle transformation pathway was prevalent. The ratios of elemental to oxidized mercury (approximately 4:1) were similar for $O_2$–CO$_2$ and air combustion.

Introduction

Coal is one of the cheapest and most abundant reserve sources of energy. Approximately 60% of the total electricity in the United States is generated by coal combustion.1 Because of the large amount of coal burned, emissions from coal combustion are significant and of potential environmental concern. The major environmental issues associated with coal combustion are potential climate change due to emissions of carbon dioxide (CO$_2$); emissions of nitrogen oxides (NO$_x$), fine particles (sizes less than 1 μm), and mercury to the atmosphere. Because of the potential impact of global warming, capture of CO$_2$ from coal combustion exhausts is receiving attention. However, the volume fraction of CO$_2$ in a conventional coal combustion system (with air) ranges from only 13 to 15%, making it very difficult to design cost-effective capture systems. One approach to overcoming the limitation of low carbon dioxide concentration in the exhaust gas is to combust the coal in oxygen-enriched air (by removing nitrogen) and recycle the exhaust gas to serve the role of the diluent. Such a configuration would result in a carbon dioxide concentration of 95%,2–5 making it more feasible to capture CO$_2$. Other advantages include reduced volume of flue gas to exhaust, potential for increasing boiler thermal efficiency, elimination of thermal NO$_x$ (due to removal of nitrogen from the air stream), decreased conversion ratio of fuel-N to exhaust NO, and increased reduction of NO to N$_2$.6,7

Although there are clear advantages to combustion in an $O_2$–CO$_2$ environment, the impact on other pollutants, such as the submicrometer mode and mercury emission, has not yet been established. The formation of the submicrometer mode of ash in coal–air combustion systems has been studied extensively.8–11 There are two pathways for the formation of the submicrometer mode of ash in coal–air combustion: vaporization and chemical transformation via reduction and oxidation reactions. Heavy metals and organically associated cations, such as Na, Pb, Cd, and Hg, are directly vaporized from the burning coal particle. These volatile species may undergo gas-phase chemical reactions and subsequently nucleate to form new particles or condense on the surface of existing particles. Submicrometer-sized particles with a mode around 0.1 μm are formed via this pathway.8–11 The other mineral transformation pathway for nonvolatile species, such as silica, during coal combustion was...
proposed by Quann et al.\textsuperscript{10} These species with a high melting temperature are released from the burning char particle in the form of suboxides via a reduction reaction at the inclusion surface of the particle. These metals or mineral suboxides, which are more volatile than the corresponding refractory oxides, diffuse away from the parent coal particle, reoxidize, become supersaturated, and form particles by nucleation, followed by growth by condensation and collision mechanisms.

Linak and Peterson\textsuperscript{12}\textsuperscript{12} studied the effect of coal type and residence time on particle size distributions and concluded that the accumulation of particles in the submicrometer size range results from vaporization, nucleation, condensation, and coagulation. Zhuang and Biswas\textsuperscript{8}\textsuperscript{8} reported that the submicrometer size particles are initially formed by nucleation due to chemical transformation, followed by growth by condensation. Most studies have reported that the submicrometer particle formation mechanisms in coal combustion are very complex and depend on a number of factors, such as coal type, combustion temperature, fuel:air ratio, and residence time. These factors also play an important role on the final particle size distribution.\textsuperscript{9,11,13,14}

Mercury emission from coal combustion has also been an issue of great concern because of its high toxicity, difficulty in being controlled, and tendency to bioaccumulate in the environment. Despite a low concentration (1–30 µg/m\textsuperscript{3}) of mercury in the flue gas, coal combustors are the largest anthropogenic source of mercury emission in the United States.\textsuperscript{15} They contribute approximately 40% of the total mercury emitted into the atmosphere.\textsuperscript{15} The chemical forms of emitted mercury can be classified as elemental mercury (Hg\textsubscript{0}(g)), various oxidized mercury compounds (Hg\textsuperscript{2+} X(g)), and mercury in association with particulate matter (Hg(p)). Mercury is released from the coal matrix to the gas phase via a direct vaporization process. At temperatures greater than 1200 °C, mercury exists primarily in the elemental form (Hg\textsubscript{0}(g)).\textsuperscript{16,17} As the flue gas subsequently cools, the gaseous elemental mercury interacts with other combustion by-products, such as HCl, CO, NO\textsubscript{x}, and fly ash. This results in a portion of the elemental mercury being converted into other mercuric compounds, such as HgCl\textsubscript{2} and HgO.\textsuperscript{18} The fraction of each species of mercury in the flue gas varies depending on coal and flue gas composition, combustion condition, and the time—temperature profile in the combustion system. The speciation of mercury is an important aspect for appropriate choice of mercury control methodology.\textsuperscript{19}

There have been several studies on the design and evaluation of coal combustion efficiency in O\textsubscript{2}–CO\textsubscript{2} systems.\textsuperscript{3,20–23} Whereas advantages with respect to the potential for CO\textsubscript{2} capture, reduction of NO\textsubscript{x} emissions, and improvement in combustion efficiency have been demonstrated, the impacts on fine particle formation and speciation of mercury have not been studied. In this paper, a mechanistic understanding of submicrometer particle formation and mercury speciation in O\textsubscript{2}–CO\textsubscript{2} combustion is established. Comparisons with combustion in air are reported and differences are highlighted.

**Experimental Section and Methods**

**Experiment.** The experimental setup is shown in Figure 1 and consists of a coal feeding system, a tubular furnace (Lindberg/Blue M, model HTF55342C, \(T_{\text{max}} = 1200^\circ\text{C}\), Thermoelectron Corp.,

United States) with an alumina reactor tube (5.72 cm inside diameter and 121.92 cm long), a cascade impactor, and measuring systems. Pulverized Powder River Basin (PRB) subbituminous coal with a mean particle size of 50 μm is introduced into the electrically heated alumina tubular reactor by a fluidized bed coal feeder with coal feed rate of 1 g/h. The oxidant, either as air (conventional) or a mixture of oxygen, carbon dioxide, and nitrogen (varying ratios), is introduced into the combustor at a total flow rate of 1.75 L min⁻¹.

The temperature in the heated alumina tubular reactor was held constant at 1200 °C (set point) for 0.60 m around the center of the reactor. At the exit of the combustor, particle-free air, at a flow rate of 12.25 L min⁻¹, is added to quench the aerosol dynamics and chemical reactions. The cooling rate of the flue gas is ~220 °C/s. The temperature of the flue gas after dilution was approximately 40 °C. All measurements are made at the conditions at the exit of the combustor. A six-stage cascade impactor (Mark III, Pollution Control System Corp., Seattle, WA) with a final stage 50% cutoff particle size of 0.5 μm, is used to remove the large (coarse) ash particles. A slip stream (0.3 L min⁻¹) downstream of the impactor is then introduced into a real time scanning mobility particle sizer (SMPS, TSI Inc., Shoreview, MN) to determine the particle size distribution ranging from 12 to 500 nm. The submicrometer particles are also collected on Teflon filters for elemental analysis. X-ray fluorescence spectroscopy (XRF) is used to obtain the elemental concentration of 72 species. In addition, the morphology of the submicrometer particles is examined by a scanning electron microscopy (SEM, Hitachi S-4500).

A 1 L min⁻¹ flow downstream of the impactor is passed through a mercury sampling train to determine oxidized and elemental mercury concentrations. A total of 90 L of gas is sampled throughout a 90 min duration. The sampling train and technique used for gaseous mercury measurement are based on the method developed by Hedrick et al. The sampling train consists of the following five impinger solutions: 2 impingers of 1.0 M tris-buffer and EDTA for capture of oxidized mercury, 1 impinger of 10% hydrogen peroxide and 2% nitric acid for oxidizing and capture of elemental mercury, and 2 impingers of 0.05 M potassium iodide and 2% hydrochloric acid for capture of elemental mercury. The impinger solutions are analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to determine the elemental and oxidized fractions of mercury in the exhaust gas.

**Flame Temperature Calculation.** A computer code for chemical equilibrium, STANJAN, is used to calculate the equilibrium compositions and the adiabatic flame temperature. The temperature in the vicinity of the burning coal particle is assumed to be the adiabatic flame temperature. The database of thermodynamic information for various species is obtained from Wu and Biswas.

**Test Plan.** The overall objective is to understand the effects of O₂–CO₂ coal combustion on submicrometer particle formation and mercury speciation. The experimental plan is outlined in Table 1. The objective of the first set of experiments (Set I) is to compare characteristics of the submicrometer particles when N₂ from air is completely replaced by CO₂. Set II experiments are designed to study the effects of varying N₂ and CO₂ on the particle size distribution. The experiments are conducted at a fixed concentration of O₂ (20% by volume) and varying ratios of N₂/CO₂. Set III experiments are carried out to study the influence of the O₂–CO₂ ratio. Set IV experiments are designed to determine the effect of O₂–CO₂ combustion on mercury speciation. Experiments are conducted for coal combustion in air, 20% O₂/80% CO₂, and 25% O₂/75% CO₂.

### Results and Discussion

**Characteristics of Submicrometer-Sized Particles.** Set I. 

**Air versus 20% O₂/80% CO₂.** The resulting ash is classified into two fractions: a coarse mode (>0.5 μm) and a submicrometer mode (<0.5 μm). The total mass of ash formed (7 mg/g of coal) is approximately the same in both combustion in air and in 20% O₂/80% CO₂, confirming that the carbonaceous species is completely oxidized. The submicrometer/coarse ash mass fraction in air combustion is 2.5 times higher than that in the O₂–CO₂ system (Table 2). As described in the Introduction, there are two pathways (direct vaporization of volatile metals and vaporization by chemical transformation) for the formation of the submicrometer mode (Figure 2). Both pathways are a strong function of temperature. The temperature in the vicinity of the burning coal particle is higher for combustion in air than in the O₂–CO₂ system. One reason is that specific heat capacity (C_p) of N₂ is lower than that of CO₂, especially at elevated temperatures (C_p at 1200 °C: N₂ = 20.78 kJ kmol⁻¹°C⁻¹ and CO₂ = 58.84 kJ kmol⁻¹°C⁻¹). The higher specific heat capacity of CO₂ leads to a lowering of the surface temperature of the burning coal particles by approximately 400–500 °C and an increase in the ignition time of coal and char particles. The mass diffusivity of O₂ in CO₂ is lower than that of O₂ in N₂ (D_O₂/CO₂ = 1.3 × 10⁻⁴ m²/s and D_O₂/N₂ = 1.7 × 10⁻⁴ m²/s).

The coal burning process is a diffusion-limited reaction; oxygen diffuses from the bulk gas to the surface of the burning particles.

---


A lower diffusivity of O$_2$ in CO$_2$ (compared to O$_2$ in N$_2$) slows down the particle burning and heat generation rates. As diffusivity is a strong function of temperature, a lower temperature in the vicinity of the burning coal particles in the O$_2$-CO$_2$ system results in a slower diffusion rate of oxygen to the surface of the burning coal particle compared to that in air (O$_2$-N$_2$). This leads to lower vaporization and particle formation rates when combustion occurs in an O$_2$-CO$_2$ mix compared to that occurring in air. The excess carbon dioxide in the vicinity of the coal particle is also expected to alter the reaction equilibrium and slow down the burning rate. Although the adiabatic temperature represents only an ideal case, it was calculated using the equilibrium code. The estimated temperature in the vicinity of the burning coal particle (determined by STANJAN) in air is 2311 K, compared to 1772 K in the O$_2$-CO$_2$ system.

The major elemental compositions (by mass) in PRB coal ash are silicon (32%), calcium (20%), aluminum (17%), and iron (8%). The major elements are found in the submicrometer mode for both 20% O$_2$/80% CO$_2$ and air combustion, as shown in Figure 3. The mass of each elemental species found in the submicrometer ash reflects the amount of the species vaporized during the combustion of coal. Even though silicon is in higher concentration than calcium and iron in PRB coal, it is found in a lower mass fraction in the submicrometer ash particles. Silicon that is present as mineral inclusions coalesces and forms a glassy type complex during combustion. This prevents further vaporization of silicon, and it is therefore retained in the coarse ash particles.$^{27}$ The heavy metal species, such as nickel and lead, are also found in the submicrometer mode, confirming that vaporization and nucleation steps are their formation pathway. However, their mass ($\mu g/g$ of coal) in the submicrometer mode is small compared to the elements illustrated in Figure 3, and hence they do not contribute to the size distribution characteristics of ash discussed later.

The normalized masses of the vaporized elements are lower for the 20% O$_2$/80% CO$_2$ combustion compared with that of

---

From 1.53 to 1.44.

Proposed by Quann et al., a high concentration of CO2 in the air for most of the major elements, particularly calcium, iron, and silicon. Consistent with the description of the chemical transformation pathway via reduction–oxidation reactions proposed by Quann et al., a high concentration of CO2 in the bulk gas deters the chemical transformation rate of mineral oxides to mineral suboxides, as CO2 is one of the products of the reduction reaction of mineral oxide. For example, the partial pressures of SiO in air and 20% O2/80% CO2 combustion are 1.77 × 10⁻² atm and 1.46 × 10⁻⁷ atm, respectively (see Appendix A for sample calculations). For most mineral oxides, the chemical nucleation step is very fast because of a very rapid reaction of the suboxides with oxygen. However, the transformation rate of mineral oxides to suboxides is slow in a 20% O2/80% CO2 system, resulting in a slower particle formation rate. The measured elemental compositions in the submicrometer particles indicates that the change of the combustion system from air to 20% O2/80% CO2 does not alter the fraction of the major species in submicrometer particles. It only affects their amounts in the submicrometer ash.

The submicrometer particle size distributions formed under 20% O2/80% CO2 and air combustion and are shown in Figure 4. The size distribution statistics are summarized in Table 2. When N2 is replaced by CO2, the geometric mean particle size reduces from 40.3 to 29.1 nm. The total number concentration in the diluted exhaust decreases by 40% from an average of 6.39 × 10⁴ #/cm³ to 3.85 × 10⁴ #/cm³. The total particle volume decreases by 38% from an average of 1.20 × 10⁻¹⁰ nm³/cm³ to 8.17 × 10⁻¹⁰ nm³/cm³. The geometric standard deviation decreases from 1.53 to 1.44.

Because the total residence time in all tests is the same, the retardation of particle formation from both vaporization and chemical transformation pathways (shown in Figure 2) results in less time available for the growth processes, such as condensation and coagulation, for combustion of coal in an O2–CO2 mix; thus, the particles formed are not only smaller in number but also smaller in size, as observed experimentally.

The SEM pictures in Figure 5 show that the primary particles formed under both combustion conditions are spherical, which implies that nucleation and condensation mechanisms are the primary cause of formation and growth of submicrometer particles. This indicates that the change in combustion condition (i.e., replacing N2 with CO2) does not alter particle formation mechanisms, but rather the rates at which they take place. Agglomerates consisting of spherical and irregularly shaped particles are also found for both combustion conditions.

**Set II. O2–N2–CO2 System.** This is a representation of a system in which nitrogen is partially replaced with carbon dioxide. Additional tests are performed at a fixed concentration of O2 but with varying the N2:CO2 mixing ratio. The particle size distributions are shown in Figure 6 and the data are also summarized in Table 2. As the N2:CO2 ratio increases from 1:4 to 4:1, the geometric mean particle size increases from 31.2 to 40.5 nm, the total particle volume increases from 1.55 × 10⁻¹⁰ nm³/cm³ to 4.40 × 10⁻¹⁰ nm³/cm³, and the geometric standard deviation increases from 1.46 to 1.60. The total number concentrations are relatively constant for all mixing ratios (ranging between 9.22 × 10⁴ #/cm³ and 1.37 × 10⁵ #/cm³). The geometric mean particle sizes and the adiabatic flame temperatures for all mixing ratios in this set of experiments are between that of air and 20% O2/80% CO2. The results of this set of experiments are consistent with the explanation in the previous section. The coal particle surface temperature increases as the ratio of N2:CO2 increases, resulting in faster vaporization rates followed by faster particle formation and growth mechanisms.

**Set III. O2–CO2 System.** The submicrometer particle size distributions formed at different O2:CO2 ratios are shown in Figure 7. The geometric mean particle size ranges from 29.1 to 54.3 nm as the O2:CO2 mixing ratio varies from 1:4 to 4:4. The geometric mean particle size and geometric standard deviation (σg) of particle size distributions increase with oxygen concentration in the system (σg increases from 29 to 54 nm and σg increases from 1.53 to 1.73). This is attributed to the increase in oxygen volume fraction from 20 to 50%, which increases the particle surface temperature from 1772 to 2679 K.

Although the particle size distribution of submicrometer particles is shifted to larger sizes as the concentration of oxygen increases, the particle number concentration in the smaller sizes (sizes smaller than 50 nm) are similar for all studied combustion conditions. This is the result of two competing mechanisms: nucleation and condensation. The vaporized species tend to nucleate when the concentration of the small particles is below a critical concentration. When the number concentration of the smaller particles is higher than the critical number concentration, condensation dominates over nucleation.28

**Mercury Speciation.** The measured mercury concentration in the gas phase in the combustion exhaust is shown in Figure 8. For conventional air combustion (Set IV, test 1), an average of 0.1 μg/m³ is oxidized mercury, and 0.4 μg/m³ is elemental mercury. This range of speciation is consistent with values

reported in the literature. Reynolds reported that approximately 10–20% of the mercury emissions from western subbituminous coals are in the oxidized state, with the remainder in the elemental state. Lee and Srivastava reported similar speciation results in the gas phase during the combustion of PRB coal. For 25% O₂/75% CO₂ combustion, an average of 0.08 µg/m³ is oxidized mercury, and 0.38 µg/m³ is elemental mercury. For 20% O₂/80% CO₂ combustion, an average of 0.1 µg/m³ is oxidized mercury, and 0.6 µg/m³ is elemental mercury. The experimental results are averaged from four repeated tests under the same condition.

The average total gaseous mercury concentration in the combustor for the experimental condition ranges from 0.65 to 0.8 µg/m³, which is consistent with mercury content measured in coal (ranging from 0.069 to 0.108 ppm). The total gaseous mercury concentrations of both O₂-CO₂ conditions are relatively the same as that of air, indicating that the O₂-CO₂ system has no effect on the vaporization of mercury. Mercury is released via direct vaporization and not by chemical reduction-oxidation (Figure 2). The burning temperature at the surface of the coal particle is high enough in both the air and O₂-CO₂ systems to vaporize mercury from the coal matrix (boiling point of mercury is only 629 K at 1 atm). The ratio of oxidized mercury to elemental mercury for both O₂-CO₂ combustion conditions is also close to that of air, indicating that the O₂-CO₂ system has no effect on the vaporization of mercury. Mercury is released via direct vaporization and not by chemical reduction-oxidation (Figure 2). The burning temperature at the surface of the coal particle is high enough in both the air and O₂-CO₂ systems to vaporize mercury from the coal matrix (boiling point of mercury is only 629 K at 1 atm). The ratio of oxidized mercury to elemental mercury for both O₂-CO₂ combustion conditions is also close to that of air, indicating that the O₂-CO₂ system does not have a significant effect on mercury speciation at the combustor exit. The experimental results here agree well with previous studies, which show that mercury is primarily in the elemental form at high temperatures.

Conclusions

This study investigated the effects of coal combustion in an O₂-CO₂ environment on submicrometer particle formation and
mercury speciation. The combustion conditions investigated in this study represented two cases of oxygen-enriched combustion with carbon dioxide recycle: (1) complete separation of O\textsubscript{2} from N\textsubscript{2} in air and (2) partial separation of O\textsubscript{2} from N\textsubscript{2} in air. When N\textsubscript{2} is replaced with CO\textsubscript{2}, the mass, number concentration, and mean size of the submicrometer particles decrease. When N\textsubscript{2} is partially removed from the air stream, the mean particle size, mass, and number concentration increase with an increasing N\textsubscript{2}: CO\textsubscript{2} ratio. When coal is combusted at different mixing ratios of O\textsubscript{2}:CO\textsubscript{2}, mean particle size and total number concentration increase as the O\textsubscript{2}:CO\textsubscript{2} mixing ratio increases.

The vaporized mole fraction of silica is calculated by assuming that the mineral oxides undergo reduction reaction during vaporization as follows:

\[
\text{SiO}_2 + \text{CO} \rightarrow \text{SiO} + \text{CO}_2; \quad K_e = \frac{P_{\text{SiO}} P_{\text{CO}_2}}{P_{\text{SiO}} P_{\text{CO}}} \quad (1)
\]

where \(K_e\) is the equilibrium constant for the mineral oxides of interest, in this case SiO\textsubscript{2}, \(P_{\text{SiO}}\) is an equilibrium vapor pressure of silicon sub-oxide (SiO) at the surface of the coal particle, \(P_{\text{CO}}\) and \(P_{\text{CO}_2}\) are the local partial pressures of CO and CO\textsubscript{2}, respectively, and \(a_{\text{SiO}}\) is the activity of solid metal oxide (which is assumed to be \(\sim 1\)).

From stoichiometry, \(P_{\text{CO}}\) at the surface of the particle is estimated to be

\[
P_{\text{CO, surface}} = \frac{2P_{O_2, bulk}}{1 + P_{O_2, bulk}} \quad (2)
\]

where \(P_{O_2, bulk}\) is the partial pressure of oxygen in the bulk gas. Assuming that the partial pressures of O\textsubscript{2} in both the air and O\textsubscript{2}–CO\textsubscript{2} systems are equal (0.21 atm), the partial pressure of carbon monoxide at the particle surface, \(P_{\text{CO, surface}}\), is 0.33 atm for both systems. The equilibrium constant \((K_e)\) for vaporization of the selected mineral oxide is calculated from the equilibrium equation and equilibrium coefficients, obtained from Senior et al.\textsuperscript{11} as follows

\[
\ln(K_e) = A + (B \times 10^6)/T \quad (3)
\]

where \(A\) and \(B\) are equilibrium coefficients (for silicon, \(A = 18.8256\) and \(B = -5.97\)) and \(T\) is the temperature at the surface of the particle, using the adiabatic flame temperature; for air, \(T_{ad} = 2311\) K, and for 20% O\textsubscript{2}/80% CO\textsubscript{2}, \(T_{ad} = 1772\) K.

For air combustion, the mineral oxide vaporization reaction is assumed to be the only source of carbon dioxide, \(P_{\text{CO}_2}\), at the surface of coal particle.\textsuperscript{10,11} Thus, the partial pressure of silicon sub-oxide (SiO) can be calculated as

\[
P_{\text{SiO}} = (a_{\text{SiO}} K_e P_{\text{CO}})^{1/2} \text{ for air combustion} \quad (4)
\]

For O\textsubscript{2}–CO\textsubscript{2}, \(P_{\text{CO}_2}\) at the surface of the coal particle is estimated to be equal to that of bulk gas. The pressure in the combustor is assumed to be 1 atm; therefore, 80% CO\textsubscript{2} in the bulk gas results in a partial pressure of CO\textsubscript{2} of 0.8 atm. \(P_{\text{CO}_2}\) from the metal oxide vaporization reaction is negligible compared with \(P_{\text{CO}_2}\) from the bulk gas

\[
P_{\text{SiO}} = (a_{\text{SiO}} K_e P_{\text{CO}})^{1/2} \text{ for } O_2^-CO_2 \text{ combustion} \quad (5)
\]

By substituting \(P_{\text{CO}_2}\) and \(P_{O_2, bulk}\) and \(T_{ad}\) in eqs 4 and 5, the partial pressures of SiO at the surface of the coal particles are estimated to be \(1.77 \times 10^{-2}\) atm and \(1.46 \times 10^{-7}\) atm for air and 20% O\textsubscript{2}/80% CO\textsubscript{2}, respectively. This calculation shows that vaporization of mineral oxides via reduction–oxidation reactions is suppressed in the O\textsubscript{2}–CO\textsubscript{2} system because of the presence of a high CO\textsubscript{2} concentration.

\*EF060178S*