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Factors affecting the vaporisation of silica during coal combustion

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Abstract

This study has quantified the amount of silica vaporised during the combustion of five Australian bituminous coals in a drop tube furnace at two oxygen partial pressures. The coals have been analysed extensively using a wide range of analytical techniques including QEMSCAN, quantitative XRD analysis, and ICP-AES. These analyses provided the modes of occurrence of the silica in these coals. The amounts vaporised were compared with the modes of occurrence of the silica, to determine the factors contributing to its vaporisation. Three main conclusions were drawn from these experiments:

- Increasing the char combustion temperature by elevating the oxygen partial pressure from 0.21 to 0.50 atm during combustion increases the extent of silica vaporisation significantly. This is consistent with previous findings.
- The size distribution of the included quartz minerals greater than 2 μm does not affect the extent of silica vaporisation significantly,
- Qualitative measurements indicate that finely dispersed silicon-bearing minerals of a size less than 2 μm could play an important role on the vaporisation of silica. An analytical procedure to quantify these minerals is necessary to establish this relationship.
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1. Introduction

The health effects of ambient fine particulates have been studied extensively and correlations have been observed between ambient fine particulate matter concentrations and human mortality rates (e.g. [1]). Governments worldwide acknowledge these studies and as a result standards have been introduced to assist in reducing ambient fine particulate concentrations. In Australia, around 80% of the electricity is dependent on coal [2], and coal-fired power generators are increasingly being required to monitor and characterise their emissions of fine particulate matter.

Measurements of ash emitted from pulverised coal fired power stations have shown that the emitted ash typically displays a bimodal mass size distribution (e.g. [3,4]). The majority of the mass of the emitted ash is supermicron in size, while a smaller, second mode was found in the submicron size region. Later studies have confirmed the bimodal ash size distribution, and have even observed a third mode, located between the other two, consisting of ash particles of a few micrometer in size [5–7]. Fig. 1 shows an illustrative particle size distribution of ash from coal combustion.

The formation of the submicron ash is important for two reasons:

- Air pollution control devices such as electrostatic precipitators typically display a lower collection efficiency for fine ash particles (~0.1–1 μm) [4,8],
- Ultrafine particles can enter the lung and enter the body through the layer of cells lining the alveoli (air sacks) of the lung. The impact of these particles on human health is not clearly understood, however they could have an effect on human health [8].

The submicron ash from coal combustion is typically formed from the nucleation and condensation of vaporised inorganic

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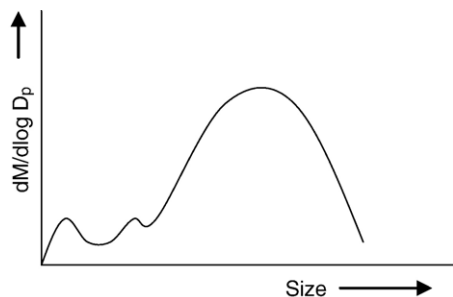*E-mail address:* rajender.gupta@ualberta.ca (R. Gupta).

Fig. 1. Illustrative ash particle size distribution.

matter [9–12]. The amount and composition of submicron ash depends on combustion conditions and coal characteristics. Although the chemical composition of submicron ash reported in the literature shows considerable variation, silicon is one of the main elements in the submicron ash. Quann and co-workers determined the submicron fume composition of the combustion products of eight coals in 20% oxygen and measured silica contents between 1.64 and 43.78% [11,13]. In a further study by the same group, the submicron ash from the combustion of eleven coals in the same combustion conditions was analysed and a silica content between 1.6 and 48.7% was determined [14]. Buhre and co-workers determined the silica content in the submicron ash from the combustion of five coals in 20 and 50% oxygen [10,15]. The silica content in the fume was between 8.9 and 20.7% for the combustion experiments in 21% oxygen, and between 21.9 and 71.9% for the combustion experiments in 50% oxygen.

2. Silica vaporisation

Silica in black coal predominantly occurs in the form of clays or quartz minerals, with decomposition temperatures typically higher than those occurring in a pulverised fuel flame [16]. In a study of the volatilisation of silica during coal gasification, Raask and Wilkins concluded that the amount of silica vaporised in coal-fired boilers could not be explained by direct vaporisation, but had to be the result of the reduction of silica to a more volatile silicon monoxide [17]. This reduction is the result of the reaction of included silica in the burning char particles with carbon or carbon monoxide to form the reduced silicon monoxide inside the burning char particle, indicated by the following chemical reactions:

$$SiO_2(s) + C(s) \Leftrightarrow SiO(g) + CO(g) \qquad (1)$$

$$SiO_2(s) + CO(g) \Leftrightarrow SiO(g) + CO_2(g) \qquad (2)$$

The gaseous silicon monoxide diffuses through the pores of the burning char particle to the outer surface. As the silicon monoxide diffuses away from the char particle and encounters oxygen, the species re-oxidises to form the original oxide. Upon cooling, the newly formed silicon dioxide condenses homogeneously to form ultrafine ash particles, in literature often referred to as fume. This fume can be scavenged by heterogeneous

condensation onto (or coagulation with) surrounding larger particles [18].

Quann and co-workers proposed a model to predict the vaporisation of refractory oxides such as silica [13]. In their model, thermodynamic equilibrium calculations were used to determine the partial pressure of the silicon monoxide inside the burning char particle based on homogeneously dispersed mono-sized silica inclusions. The model includes diffusive transport of gaseous SiO through the pores of the burning char particle to the outer surface. The model was validated with experimental results of the combustion of 14 coals in different combustion environments [12,13]. Unfortunately, no information on mineral size distribution in the coal was available at the time and the effect of mineral size inclusion on extent of vaporisation could not be determined. Eddings and co-workers applied the vaporisation model to calculate the mineral inclusion size that corresponds best with the measured fractions of vaporised ash during those experiments [19]. The calculated (mono-sized) silica inclusion size for the 14 coals varied between 10 and 20 μm. It was suggested that the model should be revised with a better model for the CO/CO$_2$ ratio inside the burning char particle, which could affect the calculated inclusion sizes.

In a study for the U.S. Department of Energy, synthetic chars doped with different-sized SiO$_2$ inclusions were burned in a drop tube furnace to determine the effect of silica inclusion size and combustion conditions on the extent of silica vaporisation [20]. The chars were burned in several oxygen concentrations (20, 40, 60 and 80%) and the mass of the resulting fume on the filter was determined to estimate the amount of silica vaporised. Three SiO$_2$ size cuts were used: 2–4, 4–6, and 12–15 μm, making up 2 and 10 wt.% of the char. Two conclusions were drawn from these experiments:

(1) The extent of vaporisation increases with an increase in oxygen concentration.
(2) The effect of inclusion size on extent of vaporisation was inconclusive; the amount of fume generated from the combustion of char doped with 10 wt.% nominal 2 to 4 μm inclusions was greater than that of 10 wt.% 4 to 6 μm sized inclusions. However, the largest amount of fume generated by the char doped with only 2 wt.% 2 to 4 μm inclusions. The study concluded that the results needed to be repeated.

Haynes calculated the vaporisation rate of silica using a more detailed model of the CO and CO$_2$ concentrations inside burning char particles [21]. The model incorporates homogeneous kinetics in pores and in the boundary layer, heterogeneous kinetics in pores, and gas-phase mass transport in char pores and in the boundary layer. Silica was assumed to be homogeneously distributed throughout the char particle, and the effect of mineral size distribution was not considered. Model predictions of silica vaporisation in different combustion conditions (oxygen concentrations) agreed well with experimental results. It was concluded that at the temperatures relevant to coal combustion, the carbothermal reduction of silica with carbon monoxide was responsible for the bulk of the