The Role of CO_2 in Mitigating the Vaporization of Metal Oxides from Coal Combustion.

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INTRODUCTION

Understanding the formation of submicron ash will become increasingly important as EPA begins setting standard limitations for the emission of hazardous air pollutants. The vaporization of minerals is proportional to the vapor pressure of CO and increases with increasing temperature. Vaporization of refractory oxides also increases in reducing atmospheres where a more volatile reduced species is formed via the reaction:

$$MO(s) + CO(g) \leftrightarrow M(g) + CO_2(g)$$

where M is a metal such as Fe, Mg, or Ca. Hence, the vaporization of refractory oxides may be suppressed by an increased CO_2 vapor pressure if the reverse reaction is important.

The effect of carbon dioxide on mineral vaporization has been studied previously, but limited data (only one coal was considered) was obtained [1]. As the effects of carbon dioxide as a greenhouse gas become more important, a proposed method of carbon dioxide sequestration is using a pure oxygen environment for coal combustion. Understanding the effect of carbon dioxide and the corresponding effects on metal vaporization are therefore of increasing importance since, in 100% oxygen environment, the carbon dioxide in the combustion products would be between 80-90%.

EXPERIMENTAL

Three coals were selected for this study. The coals were burned at 1650 K under a series of fuel-rich and oxygen-rich conditions with the balance either nitrogen or carbon dioxide as seen in **Table 1**. The oxygen concentration was varied to obtain different combustion temperatures. Nitrogen provided an inert environment for combustion. The oxygen/carbon dioxide environment allowed study of the impact of carbon dioxide on the reduction of refractory oxide metals in the submicron ash (indication of suppressed vaporization).

Oxygen, %	Nitrogen, %	Carbon Dioxide, %
0	100	0
20	80	0
50	50	0
100	2	2
20	0	80
50	0	50

Table 1. Combustion conditions vary oxygen, nitrogen, and carbon dioxide concentrations.

The three coals selected represented a distribution of type and mineralogy. Ohio (5,6,7) is a bituminous coal from the Ohio River Basin, containing moderate sulfur and low iron. Wyodak is a sub-bituminous coal from the Powder River Basin. In this coal, the elements selenium, chromium, and arsenic are largely associated with the organic matter. The last coal, North Dakota Lignite, is a low rank coal with substantial water; sulfur bound as pyrite; and is high in organically-bound calcium, magnesium, and sodium.

The experiments were performed in a drop tube furnace, illustrated in **Figure 1**. The furnace is optimized for single particle combustion experiments at temperatures up to 1750 K. Coal particles were fed to the furnace by pneumatic conveyance through a syringe feeding system at the rate of 1.2 g/hr. After combustion, the products were rapidly cooled to 390 K by the addition of nitrogen gas and passage through a water-cooled probe. An Andersen Mark II cascade impactor was located directly below the furnace for particle collection and sizing. The vertical arrangement allowed for collection of all combustion products.

All stages of the cascade impactor were lined with Durapore Millipore filters coated with Apiezon H grease, except the final filter which was ungreased. The grease prevented particle bounce from one stage to another. After a run, selected impactor states, representing the residual and submicron ash, were analyzed using Instrumental Neutron Activated Analysis (INAA).

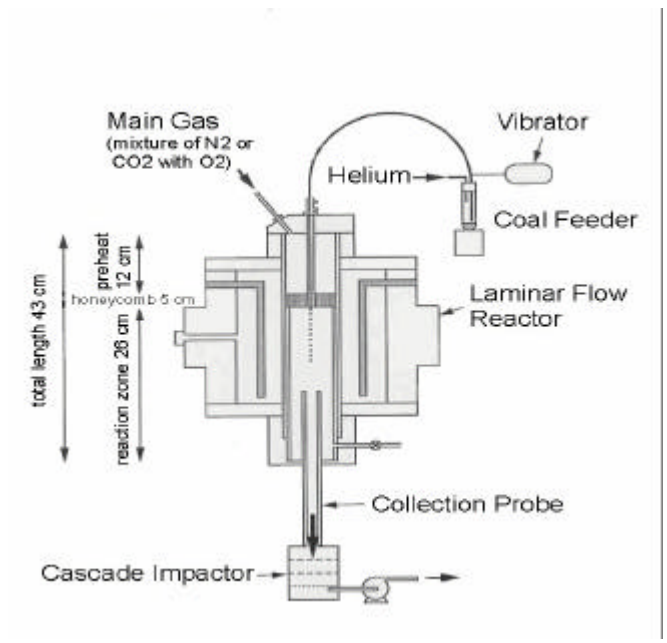

Figure 1. Schematic of drop tube furnace.

RESULTS AND DISCUSSION

As stated previously, increasing the oxygen concentration increased the combustion temperature. Using a computer model, an increase of approximately 300 K was calculated over a range of 0-100% oxygen. Quann's data confirms this calculation [1]. As shown in **Figure 2**, an increase in temperature, increased the vaporization of metals; in this case, only chromium and calcium are shown.

Carbon dioxide effects were seen on some metal vaporization, as expected. Quann found that the temperature in the drop tube furnace was unchanged when nitrogen was substituted by carbon dioxide [1]. Hence, the effects seen in **Figure 3** and **Figure 4** are most likely a result of the change in gas environment and not temperature. **Figure 3** illustrates the effect of carbon dioxide on the vaporization of the major refractory oxides. The values shown are the

fraction of each element vaporized in an oxygen/carbon dioxide environment divided by the fraction vaporized in the oxygen/nitrogen environment. For the Ohio coal, magnesium, iron, and aluminum (at the lower temperature) all showed a suppression of vaporization. In the Wyodak coal, all metals in **Figure 3** showed a suppression. The ND lignite results are mixed due to the fact that magnesium and calcium are associated with the organic material; therefore, no carbon dioxide effect was seen for these elements. Results for other trace elements will also be discussed.

Some elements, namely those not expected to form refractory oxides, should show no carbon dioxide effect. These results are shown in **Figure 4**. For example, sodium is expected to be ion exchangeable and not a refractory oxide. The halogens, chlorine and bromine, selenium, arsenic, and antimony are also not expected to demonstrate suppression of vaporization.

In the modeling of the data, it is important to fully represent the CO/CO_2 ratio. The ratio in the pores of the coal particle must be explained by the carbon/oxygen reactions, subsequent oxidation of CO, and the carbon dioxide/solid carbon reactions [2]. A Chemkin-based model, SKIPPY, has been used to predict the equilibrium between the CO and CO_2. Data from the model predictions will also be discussed in the presentation.

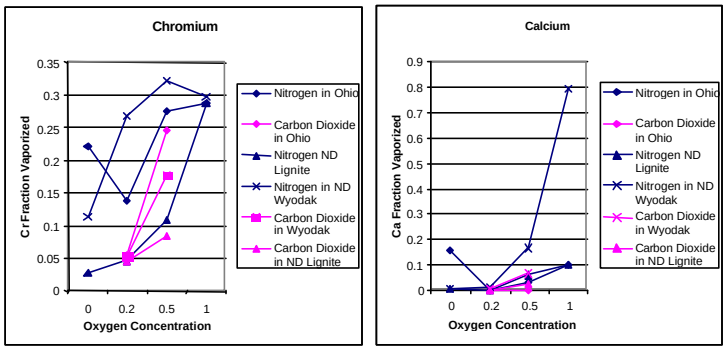

Figure 2. Temperature effects on the vaporization of chromium and calcium.

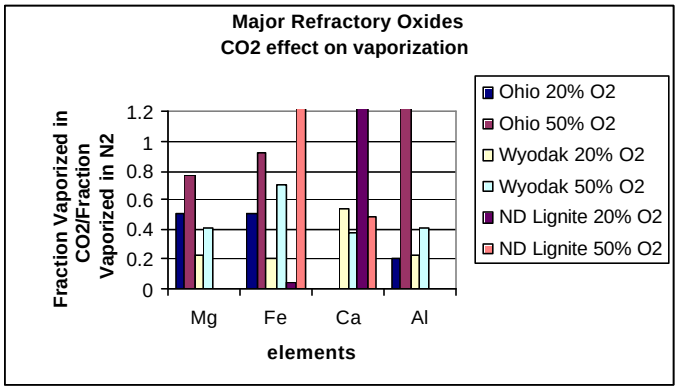

Figure 3. The carbon dioxide effect on vaporization for major refractory oxides.

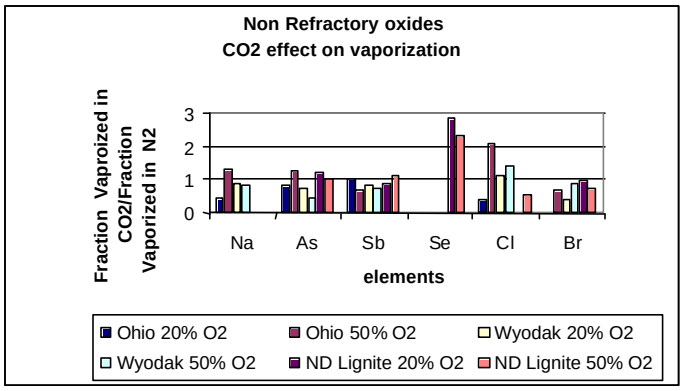

Figure 4. Carbon dioxide did not reduce the vaporization of the metals sodium, arsenic, antimony, or selenium, nor did it reduce vaporization of the halides chlorine and bromine. These elements are not refractory oxides, therefore no carbon dioxide effect was expected.

References

1. Quann, R.J. Ash vaporization under simulated pulverized coal combustion conditions, Massachusetts Institute of Technology, ScD thesis, 1992.
2. Tognotti, L, J. P. Longwell, and A. F. Sarofim, "The products of high temperature oxidation of a single char particle in an electrodynamic balance," *Proceedings of the 23rd International Symposium on Combustion*, 1990.