

TRACE ELEMENT BEHAVIOR DURING COAL COMBUSTION

J.J. Helble¹ and A.F. Sarofim²

¹PSI Technology Co., Andover MA 01810

²MIT Dept. of Chemical Engineering, Cambridge MA 02139

Keywords: Trace elements, coal combustion, partitioning

ABSTRACT

The emissions of trace elements from coal-powered processes depends to a large extent on the high temperature transformations of the trace species. In a laboratory study utilizing an Alabama bituminous coal, a Wyoming sub-bituminous coal, and a Montana lignite coal, trace element partitioning during coal combustion was examined. Experiments were conducted in an isothermal laminar flow drop tube furnace, using narrowly size-segregated coal samples to minimize particle to particle variation in the feed. In these experiments, the partitioning of the elements Zn, Mn, Cr, As, Sb, and Se among the various size fractions of ash particles was measured as a function of coal type and particle combustion temperature. Different fractions of each element were noted in the submicron ash, with Zn, As, Sb, and Se generally concentrated in the smallest ash particle size fractions.

INTRODUCTION

Title III of the 1990 Amendments to the Clean Air Act identify 189 hazardous air pollutants whose emissions may be regulated [1]. A wide variety of stationary sources, including industrial and institutional combustion sources, are to be regulated as a result of this legislation. Coal-fired electricity-generating utility power plants are currently not regulated by Title III, the hazardous air pollutants portion of the legislation. Pending the results of an EPA study of power plant emissions, however, utility boilers may also be regulated.

Of these 189 hazardous air pollutants, 11 are trace metals contained in coal. For these metals - Sb, As, Be, Cd, Co, Cr, Hg, Pb, Mn, Ni, Se - the concentration in the stack gases strongly depends upon elemental partitioning during coal combustion. For example, volatile elements such as Hg are likely to leave the boiler with the flue gases, whereas relatively non-volatile elements such as Mn are likely to be collected with the fly ash or bottom ash. These are not firm "rules", however; for any element, variations in concentration in the various effluent streams have been reported [2-5].

Many of the observed differences in partitioning have been attributed to differences in coal type. This is likely due to differences in the form of an element in coal with rank. Elements associated with clays generally associate with fly ash, whereas elements associated with the organic matrix are more likely to volatilize. Consider chromium as an example. A typical chromium concentration in U.S. coal is 15 to 20 ppm [6,7], with the elemental forms uncertain. One study identified Cr within clays as a possibility, while another suggested that

50% organic association was possible [4,6]. These differences point to possible differences in partitioning for this element.

To investigate the importance of coal rank, and therefore indirectly investigate the effect of the elemental form on partitioning, a detailed laboratory study was conducted. In this paper, results from three U.S. coals are presented.

EXPERIMENTAL

Coal Selection

Experiments were conducted with three different parent coals: Illinois #6 and Alabama Rosa (bituminous), Wyoming Comanche (sub-bituminous), and a Montana lignite. A density-separated sample of the Montana lignite, treated to remove all coal particles with a specific gravity greater than 1.8, was also investigated to look for differences in behavior arising from reduced ash content. Selected trace element concentration data for these coals are presented in Table I. For most of the elements considered in this study, concentration of the element within the coal varied by factors of 2 to 20 with coal type.

Laboratory Combustion Facility

All of the coal combustion experiments were conducted in the MIT laboratory scale laminar flow furnace [8]. A schematic diagram of this facility is presented in Figure 1. Coal particles, sized to 53/63, 75/90, or 125/150 μm by dry sieving techniques, were injected at the top of the reactor through a water-cooled feeder probe. Feed rates of 0.01 to 0.03 g/min were used, with nitrogen serving as the entraining carrier gas. Combustion occurred in the heated zone of the laminar flow reactor, with coal particle temperatures controlled by the concentration of oxygen in the bulk gas. Reactor wall temperatures were held constant at 1750 K. At the conclusion of combustion, all ash particles and gaseous combustion products were extracted with a water-cooled, nitrogen-quenched sampling probe. Nitrogen gas was also transpired through a porous metal probe liner to minimize particle losses during sampling. Particles were size segregated on-line as needed through the use of an Andersen Mark 2 eight-stage cascade impactor.

Chemical Analysis

Neutron activation analysis at the M.I.T. Nuclear Reactor Laboratory was used to determine the concentration of trace elements in all coal and ash samples examined in this study. Analysis of orchard leaves, a standard reference material obtained from NIST, was used for calibration.

RESULTS AND DISCUSSION

The variation in the concentration of selected trace elements in the submicron ash was examined as a function of coal type, coal particle size, and coal particle combustion temperature. In addition, the concentration of selected trace elements as a function of ash particle size was examined.

Trace Element Concentration as a Function of Ash Particle Size

The concentration of trace elements as a function of ash particle size was examined in a study of Wyoming Comanche sub-bituminous coal. A 75/90 μm size fraction of the coal was used in these tests. Furnace wall temperature was maintained at 1750 K, with an oxygen partial pressure of 0.30 atmosphere (balance nitrogen). Trends observed for the elements vanadium, chromium, and manganese are presented in Figure 2. Vanadium was uniformly distributed among all particle size classes, whereas chromium was slightly enriched and manganese was significantly enriched in the submicron fraction of the ash. Chromium concentrations measured for ash generated from combustion of the density segregated Montana lignite in 20% oxygen show a similar trend to the chromium from the Wyoming coal.

Enrichment in the smallest size fraction is generally taken as a sign of vaporization. This is because condensation occurs preferentially on the smallest ash particles that provide most of the surface area. Non-volatile elements generally are concentrated in the largest ash particles. The concentration of Sc, presented for comparison in Figure 2, shows behavior typically associated with a highly refractory, non-vaporizing element. From this, we conclude that for the Wyoming sub-bituminous coal, 1) manganese vaporizes during combustion and condenses on the smallest ash particles; 2) chromium may partially volatilize during combustion; and 3) vanadium remains associated with the larger fly ash particles and hence is relatively non-volatile.

Effect of Combustion Temperature

At the gas temperatures considered in this study, the combustion of pulverized coal is controlled by the diffusion of oxygen to the particle surface at the gas. The rate of combustion and hence the coal particle temperatures are therefore affected by the flux of oxygen to the surface, which in turn is controlled by the partial pressure of oxygen in the gas. Thus, by increasing oxygen partial pressure, the coal particle combustion temperature can be raised accordingly. Measurements and calculations have indicated that coal particle temperatures may increase from approximately 1900 to 2000 K in 20% oxygen to as high as 2600 to 2800 K in 80% oxygen [8].

The effect of coal particle combustion temperature on trace element concentration in the submicron ash was investigated in a study of the Wyoming coal. Results obtained for the elements V, Cr, As, and Sb are presented in Figure 3. Concentrations of Sc are again presented as an example of a non-volatile element. Vanadium, chromium, and scandium concentrations all increased with increasing oxygen concentration indicative of relative non-volatility. Arsenic and antimony concentrations, however, decreased with increasing temperature. This suggests that the majority of each of these elements vaporized at relatively low temperatures. The reduction in concentration is a diluent effect, resulting from additional vaporization of refractory species at higher temperatures.

Effect of Feed Coal Particle Size

Trace element concentrations in the Montana lignite coal and combustion-derived submicron ash as a function of coal particle size are presented in Figure 4. Little difference was noted in the concentration of these elements in the coal or the ash for most elements. Chromium concentrations in the submicron ash, however, decreased as larger coal particles

were burned. This suggests that chromium in the largest coal particles was either retained by aluminosilicate minerals (ash particles), or was present in a more refractory form initially.

Effect of Coal Type

Enrichment of trace elements in the submicron ash was examined for the three parent coals considered in this study. As shown in Figure 5, enrichment was typically lowest for the sub-bituminous coal. Arsenic and vanadium were most volatile in the bituminous coal, whereas chromium was most volatile in the lignitic coal. For a given element, differences in enrichment factor as a function of coal type suggest differences in volatility. This in turn suggests differences in the predominant form of the element in the parent coals.

ACKNOWLEDGEMENTS

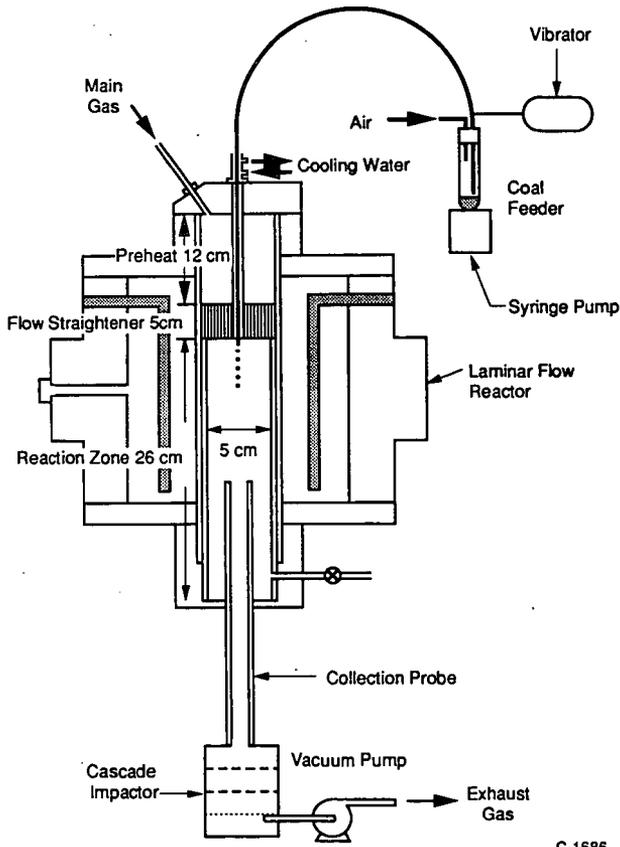
The authors acknowledge the National Institute for Environmental Health Science, the National Science Foundation, and DOE/PETC for their support of this project.

REFERENCES

1. Stensvaag, J.M., "Clean Air Act 1990 Amendments: Law and Practice," Wiley Law Publications, New York (1991).
2. Brooks, G., Radian Corporation Final Report submitted to the US EPA under contract number 68-02-4392, Report No. EPA-450/2-89-001 (1989).
3. Edwards, L.O., Muehla, C.A., Sawyer, R.E., Thompson, C.M., Williams, D.H., and Delleney, R.D., "Trace Metals and Stationary Conventional Combustion Processes," EPA Report No. EPA-600/S7-80-155 (1981).
4. Smith, R.D., *Progr. Energy Combust. Sci.* 6, 53 (1980).
5. Davison, R.L., Natusch, D.F.S., Wallace, J.R., and Evans Jr., C.A., *Env. Sci. and Tech.* 8(13), 1107 (1974).
6. Finkelman, R.B., in *Organic Geochemistry*, Engle, M., and Macko, F., eds., Plenum Publishing Co. (1992).
7. Raask, E., *Progr. Energy Combust. Sci.* 11, 97 (1985).
8. Helble, J.J., Ph.D. Thesis, M.I.T. Department of Chemical Engineering, May (1987).

Table 1. Coal Trace Element Data

| | Alabama Bituminous (75/90 μm) | Wyoming Sub-bituminous (75/90 μm) | Montana Lignite (75/90 μm) | Density- Graded M. Lignite* |
|---|---|---|--|-----------------------------------|
| Ash (wt%, dry) | 7.3 | 5.2 | 6.9 | 5.9 |
| Trace elements (ppm by weight of coal) | | | | |
| Mn | 20 | 25 | 78 | 66 |
| Cr | 14 | 11 | 3.8 | 6.1 |
| As | 30 | 1.6 | 4.0 | - |
| Sb | 1.4 | - | 0.6 | - |
| Se | - | - | 0.5 | - |
| Co | 9.2 | 2.4 | 0.9 | - |
| V | 17 | 16 | 5 | - |
| Zn | 23 | - | 8 | - |
| U | - | 0.9 | 0.5 | - |



C-1686

Figure 1. Laminar-entrained flow reactor used for combustion experiments.

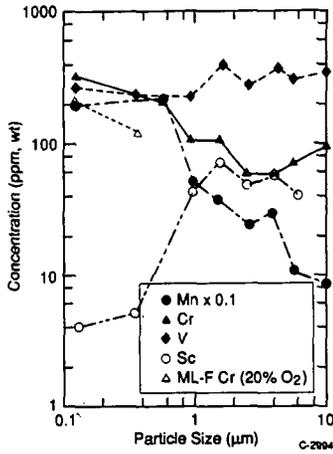


Figure 2. Concentration of trace elements in ash as a function of ash particle size for Wyoming and Montana coals. 75/90 μm, 1750 K, 30% O₂ except as noted.

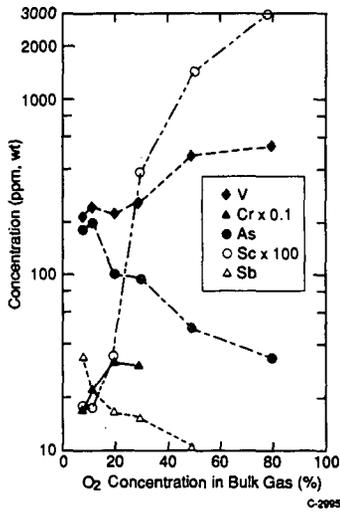


Figure 3. Concentration of trace elements in ash as a function of oxygen partial pressure. Wyoming coal, 75/90 μm, 1750 K.

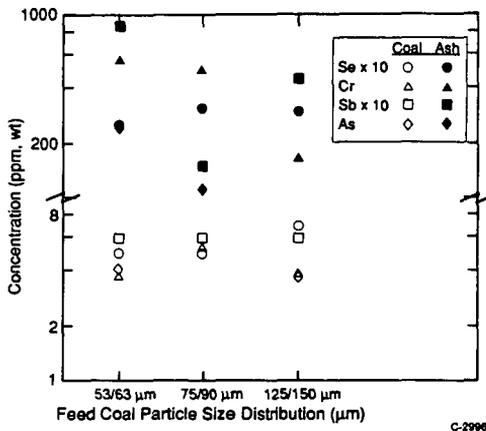


Figure 4. Concentration of trace elements in Montana lignite coal and ash as a function of coal particle size. 1750 K, 20% O₂.

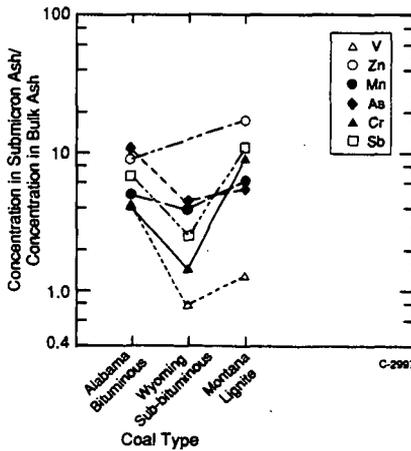


Figure 5. Relative concentration of trace elements in submicron ash as a function of coal type. 75/90 μm, 1750 K, 30% oxygen except Montana coal (20%).