Carbon Dioxide Effects on Metal Vaporization during Coal Combustion

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Abstract

Coal combustion products may take one of two forms. Residual ash (> 1 micron) is formed by particle shrinkage and breaking during combustion. Some material will vaporize and later recondense. During recondensation, these molecules have a high affinity for submicron particles because of the large surface area to volume ratio.

It is desirable for the inorganic material to remain in the residual ash so that it can be effectively filtered from flue gas. The size partitioning of metals in the ash may be altered by manipulating the combustion atmosphere. One hypothesis is that the vaporization of the refractory oxides that dominate the mass of the submicron particles is governed by the following:

$$MO(s) + CO(g) \leftrightarrow CO2(g) + M(g)$$

where M signifies a metal. Increases in the partial pressure of the carbon dioxide drive the reverse reaction, decreasing the rate of vaporization of metals. This study uses a series of atmospheres with varying oxygen concentrations and either nitrogen or carbon dioxide as the balance. Experiments have been done on several coals and a decrease in metal vaporization was seen when carbon dioxide was present. These results are being used to evaluate a kinetic model of metal reactions during coal combustion.

Introduction

Coal Combustion products may have several fates. They may fragment and drop to the bottom as super micron residual ash, become vaporized and recondense as submicron particles, or they may escape as vapor in the outgoing flue gas. It is known that vaporized molecules recondense preferentially to the submicron particles because of the large surface area to volume ratio.

In the upcoming years, the EPA will begin regulating a number of combustion products identified as hazardous air pollutants by the Clean Air Act of 1990. When the EPA sets these regulations, the utility companies of this country will need to put in place control strategies to meet the new standards. In order to prevent the costly trial and error approach, it will be necessary to have a clear understanding of the behavior of toxins in combustions systems. There is currently a broad gap in our understanding of metals in combustion. With more complete informations, we will be able to develop and implement new control technology.

Most of the particulate matter from exhaust streams of coal fired boilers is already filtered. Large particles are easily collected in baghouses and with electrostatic precipitators, however, the submicron particles present a more difficult problem. Because these small particles pass through collection systems currently in use, a means of limiting the concentration of hazardous material in the submicron ash would be a favorable way to comply with new regulations. A method of preventing metal vaporization in the combustion zone would have a considerable impact toward lowering emissions. In an attempt to characterize the behavior of metals in a coal combustion system. This study focused on the effects of using carbon dioxide in the combustion system.

Approach

All experiments were conducted in an Astro Industrial Model 1000-3560 drop tube furnace. The furnace is optimized for single particle, non-sustained combustion at temperatures up to 1750 K. It is electrically heated by a graphite heating element, which is separated from the combustion zone with an alumina silicate muffle tube. Combustion gases pass through a honeycomb flow straightener at the furnace entrance to ensure laminar flow. Because combustion is diffusion limited, the local atmosphere of the burning particle may be much different from that of the bulk gas. Oxygen is quickly depleted near the particle, resulting in locally reducing conditions. Coal particles enter the furnace by gas entrainment through a syringe feeding system.

We used three coals which represent variations in type and minerology. Ohio (5 6 7) is a blend of coals from three seams from the Ohio River Basin. It is a bituminous coal with moderate sulfur and low iron content. A similar coal blended from just two seams is currently being used in industry. Wyodak is a subbituminous coal from the Powder River Basin. It is an important steam coal. In the Wyodak coal, the elements selenium, chromium, and arsenic are largely associated with the organic matter. The third coal, North Dakota Lignite is a low ranking coal burned at a mine-to-mouth utility. It has substantial water, sulfur bound as pyrite, and is high in organically bound calcium, magnesium, and sodium.

Before combustion, the coals were sized according to ASTM sieving methods. Sizing was necessary because residual ash from ultra-fine particles would have been collected in the submicron range along with submicron particles formed through condensation. Very large particles can clog the feeding system. To limit these problems, the size range of 53-74 microns was chosen. As moisture can also cause clogging in the feeding system, the coals were dried according to ASTM methods.

The coals were burned at 1700 K under a series of fuel rich and oxygen rich conditions (table 1). The coal was entrained in helium to increase diffusion of the main gas, which entered adjacent to the coal, and was fed at a rate of approximately 0.02 grams of coal per minute in 5 milliliters per minute of helium. Below the honeycomb flow straightener, the particles contacted the main gas, which flowed at 6 liters per minute. The combustion atmosphere varied from 0-100% oxygen with the balance being either nitrogen or carbon dioxide. The nitrogen provided an inert environment for the reaction. Carbon dioxide was used to investigate the governing reaction:

$$MO(s) + CO(g) = CO2(g) + M(g) \qquad \text{reaction 1.}$$

where M represents a metal species. Carbon dioxide was expected to drive the reverse reaction, thus keeping metals in their less volatile oxidized state, and may also affect the particle temperature. The impact of the carbon dioxide is particularly important since early interpretations of the vaporization data did not properly account for the gas composition in the pores. This has been pointed out by Haynes who has developed a model to account for surface and gas phase reactions on the carbon monoxide--carbon dioxide ratio. This model will hopefully be used to analyze the data presented here.

The vertical alignment of the furnace ensured that all combustion products were available for analysis with no loss in the reactor. Before beginning any experiments, the furnace alignment was checked at room temperature. Coal was entrained with all gases entering, and 99% of coal fed was collected below the furnace.

After combustion, the particles were rapidly cooled to between 120°C and 140°C by addition of 21 liters per minute of nitrogen gas through a water-cooled probe. An Andersen Mark II cascade impactor, located directly below the furnace, collected and sized the particles. Material can be lost in the impactor due to particle bouncing and re-entrainment to lower stages. To minimize these losses, all stages of the impactor were lined with Durapore Millipore filters coated with Apiezon H grease, except the final filter, which was ungreased. This grease was chosen because it is low in metal contaminates. For application, the grease was diluted with toluene and a thin film was applied with an airbrush. The filters were then dried overnight at 120°C and the mass was recorded.

The time of experiments was from 10 to 45 minutes depending on the burning conditions. This time length was selected to allow maximum particle collection without overloading the cascade impactor. After collection, the stages were all weighed. Weights were used to determine mass balance of system and to find the breaking point between the residual and submicron ash.

The reaction rate constant k was approximated as a linear function of temperature, where

$$\frac{\partial x_i}{\partial t} = -k \cdot x \qquad \text{equation 1.}$$

and

$$k = C_1 \cdot \frac{1}{T} + C_2 \qquad \text{equation 2.}$$

Coefficients 1 and 2 are presented in table 2.

Results and Conclusions

From a visual analysis, it was clear that the carbon burned out completely at oxygen levels of 50% and 100%, and near completely at 20% oxygen. This was seen by color, where white ash indicated complete carbon combustion. The bimodal ash distribution was obvious for all tests, except at 100% oxygen, where there was no clear separation and all stages were analyzed with INAA. This is a nondestructive method, which measures the concentration of most elements with molecular weights larger than that of sodium. The mass of submicron collected when carbon dioxide was used as the inert gas was consistently less than when nitrogen was used. This was a first indication than carbon dioxide was indeed reversing the governing reaction.

The color or the super-micron ash ranged from black to powdery white depending on the extent of the combustion. The submicron ash showed a much greater variation in color, an indication of the effects of combustion condition on vaporization. Ash collected under pyrolyzing conditions had a greenish color. At 20% oxygen, the ash was a dark gray, and at 100% oxygen, the oxidizing atmosphere was manifest as reddish ash.

For the Ohio coal, the residual ash was collected primarily on stage 0 of the impactor and all submicron ash was collected on the final filter. With North Dakota Lignite, the residual ash was collected on stages 0-3. Both stages 0 and 3 were analyzed with INAA along with the final filter, which had collected the bulk of the submicron ash. The ash from the Wyodak coal had a similar collection pattern and again stages 0, 3, and the final filter were analyzed.

Information on 32 elements with atomic weights greater than 20 amu was obtained through INAA. All information is given as the fraction of an element in the raw coal collected in the ash. The data presented here is preliminary and will be ammended as more analysis results are obtained.

The fraction of the major elements collected in the submicron ash was decreased in the presence of carbon dioxide. Iron and magnesium were reduced for the Ohio coal (figure 1. a and b), sodium was reduced in the ND Lignite (figure 1. c), and with the Wyodak coal, iron, magnesium, aluminum, and sodium were all reduced (figure 1. d-g).

Several significant minor elements were also reduced in the submicron ash by using a carbon dioxide rich atmosphere. These include manganese, chromium, and zinc for the Ohio coal (figure 2). From the ND Lignite, cesium, manganese, chlorine, bromine, chromium, and molybdenum were reduced (figure 3). The Wyodak coal showed reduction of many of these along with some other interesting elements which included arsenic, zinc, antimony, and barium (figure 4).

Mercury levels in the submicron ash showed the same pattern with the Ohio coal (figure 5), however the carbon dioxide effect on mercury can be explained by the role of soot in the ash. At lower oxygen concentrations, the carbon content of the ash is increased. Because of its reactivity with carbon, the vapor phase mercury is collected with with the submicron ash.

This data supports the hypothesis that the carbon dioxide controls vaporization rates for metal species according to the governing reaction. The carbon dioxide is lowering the reaction constant, however the affect cannot simply be explained with emperical models because of the intricacies of the carbon dioxide reactions. Past research has assumed that during combustion in an oxygen/nitrogen atmosphere, all the the vapor phase carbon was present as carbon monoxide. At moderate temperatures, that was a reasonable assumption, however at high temperatures, the CO/CO2 ratio decreases as some solid carbon converts to carbon dioxide at the particle surface. In the pores, the CO/CO2 has a different equilibrium from the reaction:

$$CO + 1/2\ O2 = CO2\ . \qquad \text{reaction 2.}$$

The third parameter affecting the CO/CO2 balance is the boundary condition, which can manually be controlled. This study has been an investigation of the CO/CO2 ratio in the boundary layer. Burning in an atmosphere of carbon dioxide serves to decrease the CO/CO2 ratio to levels that can decrease metal vaporization according to reaction 1. While much of this reduction is due to the governing reaction. Temperature affects come into play for elements not present as metal oxides.

The previous studies by Quann have attempted to model these effects for a limited number of metals. The usefulness of these studies is limited, however, because of the simplified approach to the equilibrium of gaseous species. Quann's model was based on an assumption that all CO2 was produced during reaction 1, therefore the partial pressure of CO2 was equal to the partial pressure of the metal species when burning in an oxygen-nitrogen atmosphere. This assumption has come under scrutiny by Haynes, who pointed out the relevance of the other mechanisms for CO2 formation.

The data collected in this study will be applied to a model similar to one developed by Haynes, which accounts for the full equilibrium between carbon monoxide and carbon dioxide. The model also considers many other reactions taking place in the combustion zone, and involves the diffusion of gases into the particle and combustion products away from the particle. From this information, predictions of metal behavior in combustion will be better predicted.

Tables and Figures

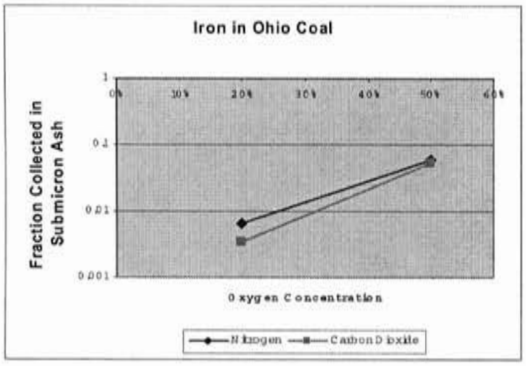
Oxygen	Nitrogen	Carbon Dioxide
0%	100%	0%
20%	80%	0%
50%	50%	0%
100%	0%	0%
20%	0%	80%
50%	0%	50%

Table 1. The coal is burned under a series of oxidizing and reducing conditions where oxygen varies from 0-100% with the balance as either nitrogen or carbon dioxide.

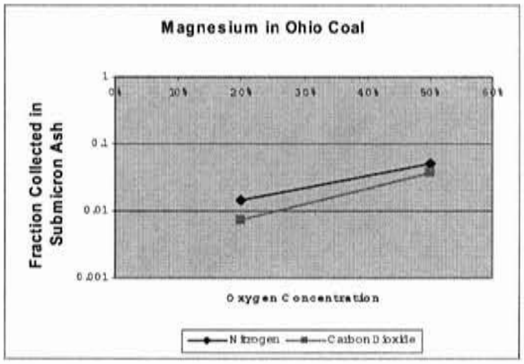
Element	C1	C2		Element	C1	C2
Mg	-20237	4.2863		Br	13167	9.1557
V	-17945	4.6051		Co	-8648.8	0.2441
Al	-18472	0.4211		La	-13928	1.2371
Na	1132.1	2.2685		As	-6084.1	0.3981
Ti	-36479	8.8646		Ce	-17421	2.9604
Mn	-22592	6.082		Nd	-154884	47.179
Sr	-14294	2.0825		Mo	-15034	2.0762
Ca	-16580	1.4977		Sm	-18510	1.4018
Ba	-30429	7.3474		Sb	-1587.6	1587.6
Sc	16402	10.526		Zn	-2812.1	2.7255
Cl	9260.9	4.1612		Cs	31243	18.144
Cr	7002.1	0.0652		Hg	-1230	3.0218
Fe	-26103	6.6511		Au	2059.8	8.3436

Table 2. The coefficients for the rate constant approximations are determined from data on temperature increases in the furnace.

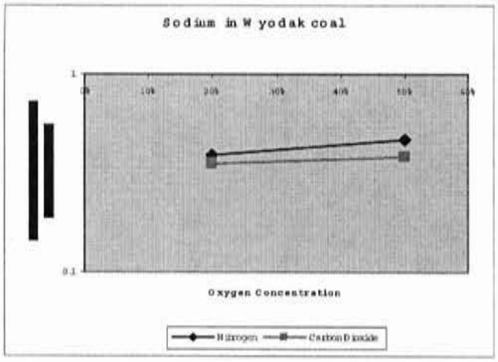
a)


Iron in Ohio Coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0.001
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

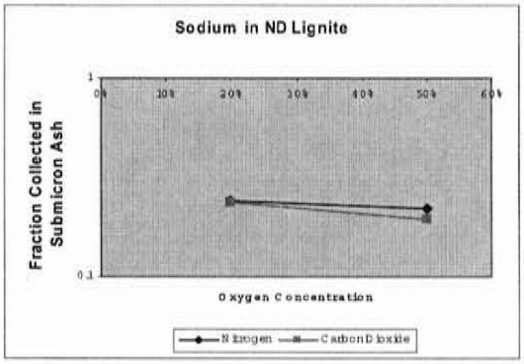
b)


Magnesium in Ohio Coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0.001
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

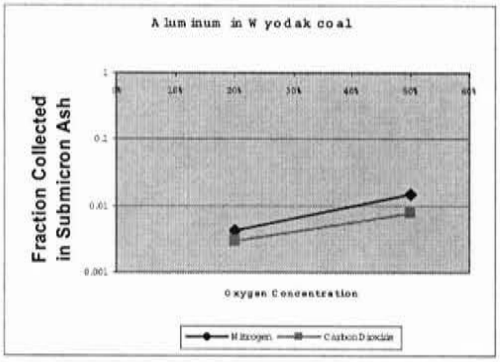
c)


Sodium in Wyodak coal
[redacted]
1
0.1
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

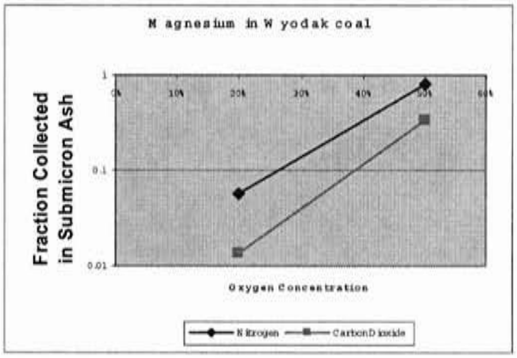
d)


Sodium in ND Lignite
Fraction Collected in Submicron Ash
1
0.1
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

e)


Aluminum in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0.001
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

f)


Magnesium in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

g)

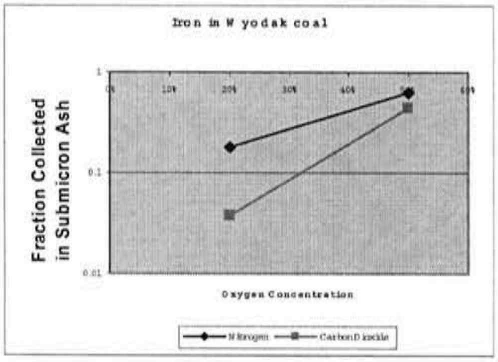

Iron in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

Figure 1. The addition of carbon dioxide to the combustion system decreases the vaporization of the major elements. Iron and magnesium were reduced for the Ohio coal (a and b), sodium was reduced in the ND Lignite (c), and with the Wyodak coal, sodium, aluminum, magnesium, and iron were all reduced (d-f). This is expected for refractory oxides because carbon dioxide drives the reverse reaction:
$MO(s) + CO(g) = M(g) + CO_2(g)$.

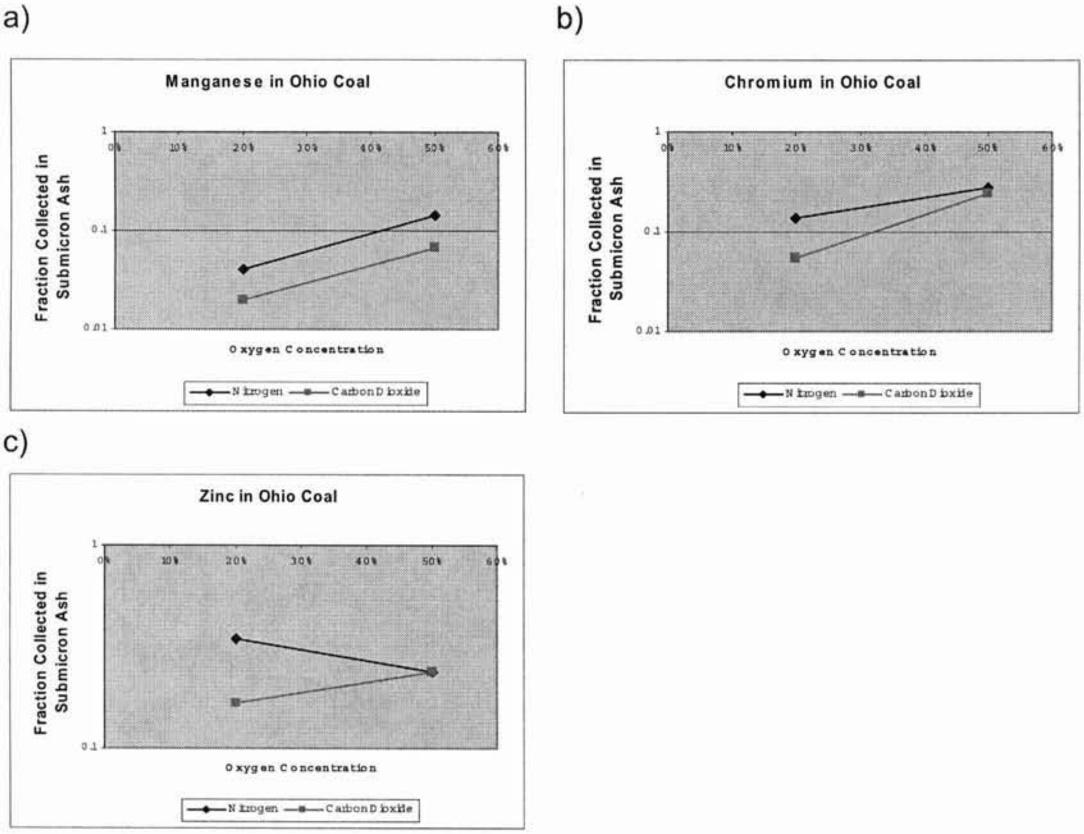
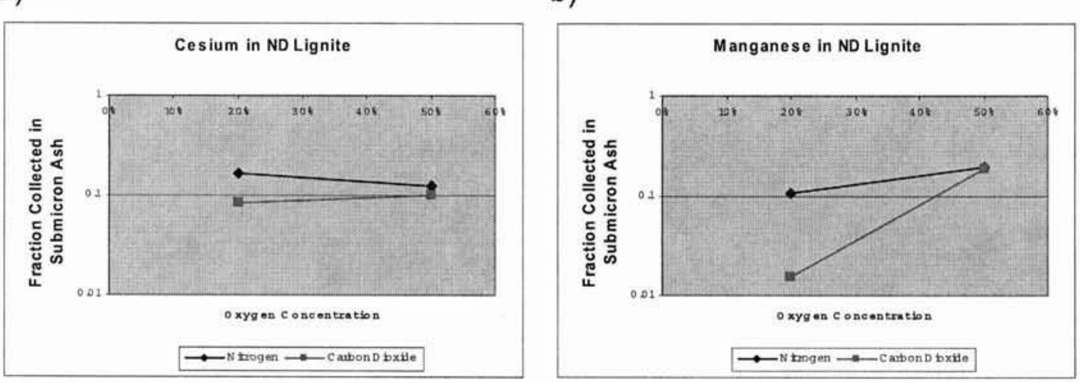

a)
b)
c)

Figure 2. Several minor elements are also reduced by the addition of carbon dioxide. These include manganese, chromium, and zinc for the Ohio coal (a-c).


a)
b)

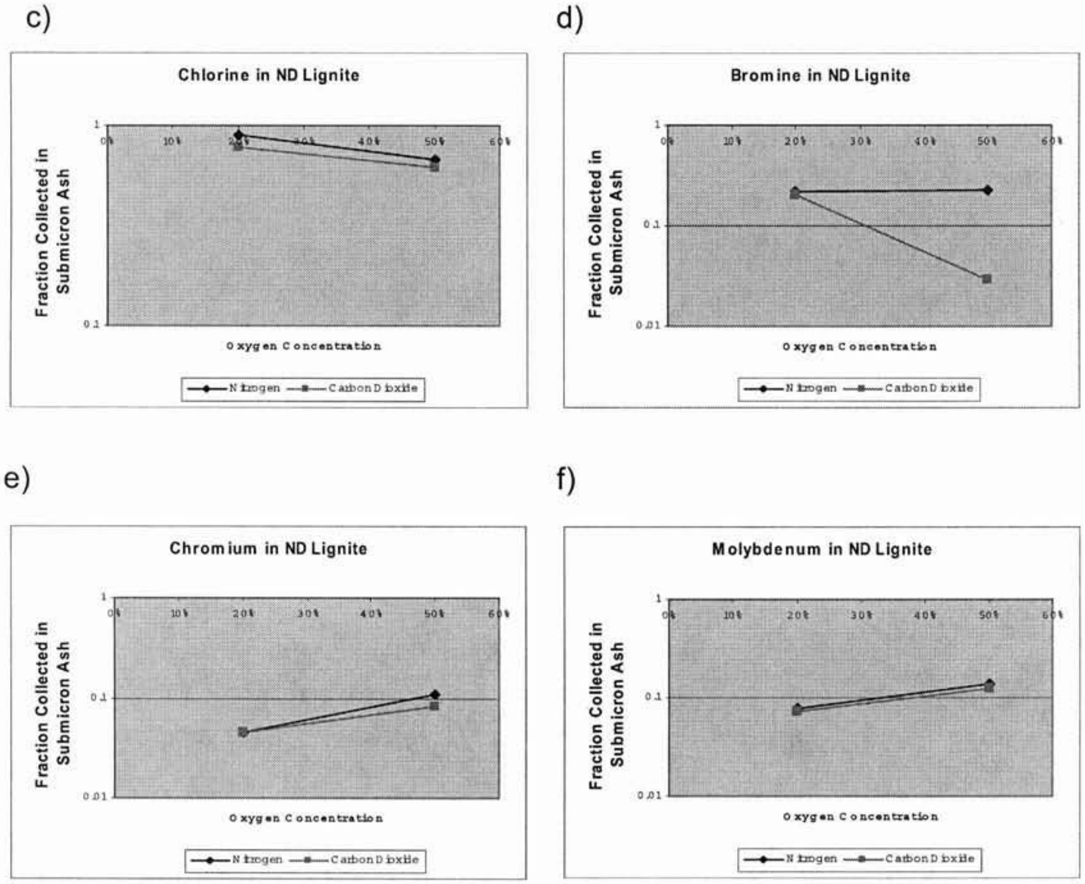
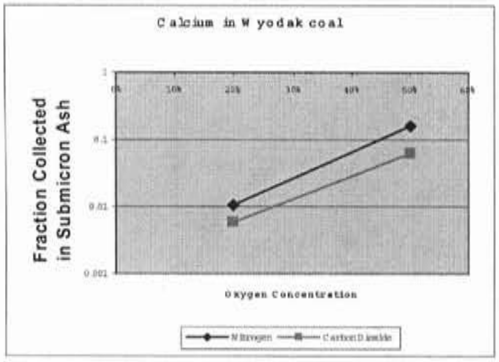
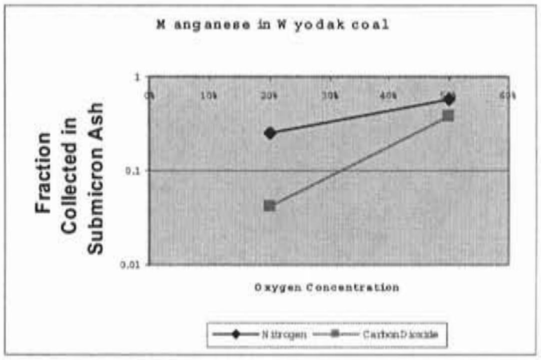


Figure 3. From the ND Lignite, the minor elements cesium, manganese, chlorine, bromine, chromium, and molybdenum, were reduced with the addition of carbon dioxide.

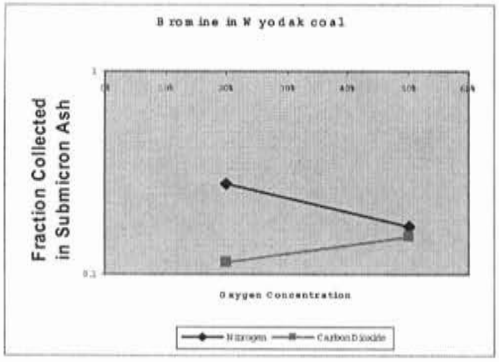
a)


Calcium in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0.001
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

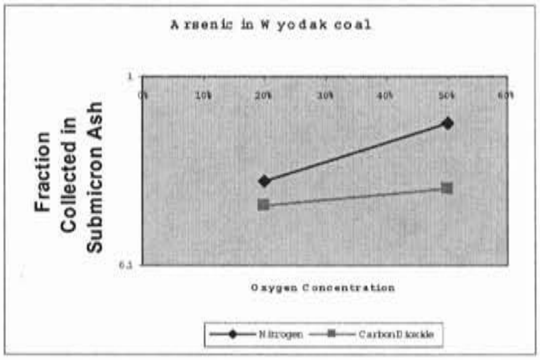
b)


Manganese in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

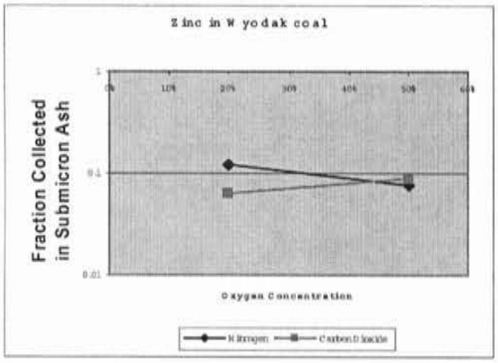
c)


Bromine in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

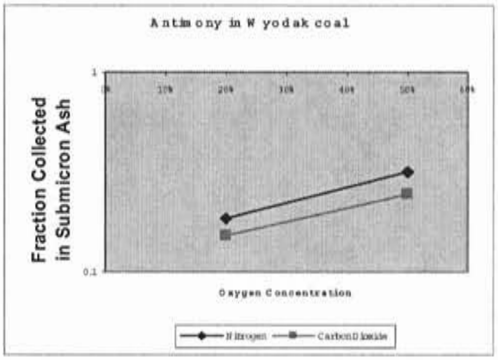
d)


Arsenic in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

e)


Zinc in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

f)


Antimony in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

g)

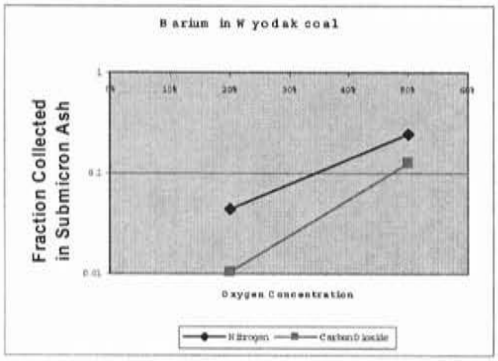

Barium in Wyodak coal
Fraction Collected in Submicron Ash
1
0.1
0.01
0%
10%
20%
30%
40%
50%
60%
Oxygen Concentration
Nitrogen
Carbon Dioxide

Figure 4. The Wyodak coal showed reduction of many of the minor elements reduced for the other coals including calcium, manganese, and barium. Several other other elements were also reduced such as arsenic, zinc, antimony, and barium.

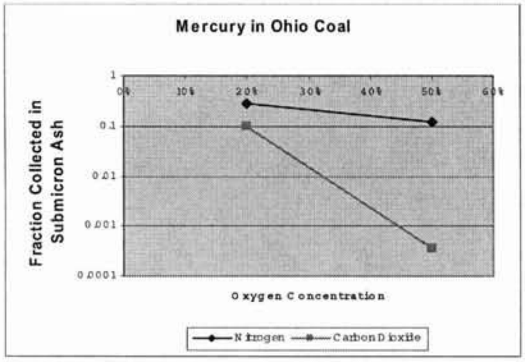


Figure 5. Mercury from the Ohio coal shows a decrease in capture on submicron particles with carbon dioxide. This is not due to the governing reactions, but is associated with the soot fraction of the particles, and absorption of mercury on carbon.

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