**NO_x, Fine Particle and Toxic Metal Emissions from the Combustion of Sewage Sludge/Coal
Mixtures: A Systematic Assessment.**

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ABSTRACT

This research project focuses on pollutants from the combustion of mixtures of dried municipal sewage sludge (MSS) and coal. The objective is to determine the relationship between 1) fraction sludge in the sludge/coal mixture, and 2) combustion conditions on a) NO_x concentrations in the exhaust, b) the size segregated fine and ultra-fine particle composition in the exhaust, and c) the partitioning of toxic metals between vapor and condensates phases, within the process. To this end work is progress using an existing 17kW downflow laboratory combustor, available with coal and sludge feed capabilities. The proposed study will be conducted in concert with an existing ongoing research on toxic metal partitioning mechanisms for very well characterized pulverized coals alone. Both high NO_x and low NO_x combustion conditions will be investigated (unstaged and staged combustion). The proposed work uses existing analytical and experimental facilities and draws on 20 years of research on NO_x and fine particles that has been funded by DOE in this laboratory. Four barrels of dried sewage sludge are currently in the laboratory. Insofar as possible pertinent mechanisms will be elucidated. Tradeoffs between CO₂ control, NO_x control, and inorganic fine particle and toxic metal emissions will be determined.

For the Fifth Quarter of this project we focus on determining whether certain trace metals are associated with certain major species, such as calcium and iron. To this end we present data showing correlations between As, Se, and Sb and major species, such as Ca and Fe. Conversely, lack of correlation between trace metals and elements, such as aluminum can also be used to infer lack of chemical association.

TABLE OF CONTENTS

INTRODUCTION	5
EXPERIMENTAL FACILITIES	6
EXPERIMENTS PERFORMED	6
EXPERIMENTAL RESULTS AND DISCUSSION (CONTINUED)	6
FUTURE WORK	8
REFERENCES	8
FIGURES	9

INTRODUCTION

Municipal sewage sludge (MSS) is formed during wastewater treatment. Sludge is the largest by-product of wastewater treating plants and its processing and disposal represent one of the most environmentally challenging aspects of the wastewater treating process [1]. As discharged, the sludge is contained in a dilute (0.25 to 12 wt%) aqueous suspension and contains hazardous compounds. A description of how sludge is generated can be found in [1].

One of the options currently being considered to improve the treatment of this sludge is a process involving heat treatment (to render the sludge biologically inactive) followed by dewatering, drying, pulverizing, and combustion [2]. The advantages of this combustion process are: a large reduction in disposal volume, thermal destruction of toxic organics, and recovery of the energy value of the carbon sources in the sludge [1]. However, there are a number of potential disadvantages including NO_x formation (due to the high nitrogen content of most MSS), handling of the raw material (due to the toxicity of metals and dioxins in the feedstock), possible boiler slagging and fouling problems (due to the high inorganic content of the feedstock), and the release of toxic trace elements into the environment [3].

A study was conducted to investigate the partitioning characteristics of selected trace elements during the combustion of a dried, treated (Swiss Combi Process), and pulverized MSS at commercially relevant temperatures (i.e. combustion zone and post-combustion zone temperatures similar to those expected in commercial combustors). The objectives of this study were:

- to quantify the partitioning of selected major inorganic (silicon, iron, calcium, and aluminum) and trace elements (zinc, arsenic, selenium, and antimony) during combustion of MSS in a natural gas flame
- to quantify the partitioning of selected major inorganic (silicon, iron, calcium, and aluminum) and trace elements (zinc, arsenic, selenium, and antimony) during co-combustion of MSS with a well-characterized bituminous coal (Ohio 5/6/7 blend)
- to identify mechanisms where possible for trace element vapor-to-solid phase partitioning
- to explore synergistic effects for co-combustion of MSS with coal

EXPERIMENTAL FACILITIES

These have been described in the Second Quarterly Report 40838R02.

EXPERIMENTS PERFORMED

These have been described in the Second Quarterly Report 40838R02, and consist of ash particle samples withdrawn from flue gases arising from combustion of

- Natural gas only:
- Gas + MSS:
- Coal Only:
- Coal + MSS:

The coal is an Ohio blend coal described previously (Report 40838R02) and the composition of dried municipal sewage sludge (MSS) has also been presented previously, in that same report.

EXPERIMENTAL RESULTS AND DISCUSSION (CONTINUED)

Temperature Profiles and Particle Size Distributions are described in the Second Quarterly Report 4083R02. Results describing partitioning of major and trace metal constituents through the particle size distribution have been described in the Third Quarterly Report 4083R03. Interpretation in terms of surface reaction and condensation mechanisms is found in Fourth Quarterly Report 4083R04.

Surface Reaction Mechanisms

The particle size dependence analysis suggests that surface reaction (or pore diffusion in porous particles) controls vapor-to-solid phase arsenic partitioning (see Fourth Quarterly Report 4083R04). Arsenic, selenium, and antimony volatilized during coal combustion are believed to form oxy-anions, predominantly of the forms As_2O_3 , SeO_2 , and Sb_2O_3 [4-6]. To explore the possibility of these vapor-phase oxy-anions reacting with cations, the differential distribution of the trace elements can be compared to the differential distributions of the cations to see if a correlation exists (Fig. 1). For the “Gas + MSS” profile, the cation distribution curves are very similar. All three trace element distributions appear to follow these profiles reasonably closely in the supermicron region and less closely in the submicron region. For the submicron region, the trace element distributions most closely resemble the silicon distribution which implies that vapor-to-solid phase partitioning in this region is not controlled by surface reaction since these oxy-anions are more reactive with active calcium and iron cation surface sites than silicon.

For the “Coal + MSS” profile, the cation distribution curves are also similar but there are more discernable differences than with the “Gas + MSS” profiles. Considering the entire profile, the three trace element profiles appear to follow the calcium profile more closely than the silicon and iron profiles.

To examine the results more carefully, the distributions were decomposed into their submicron ($d_p < 1$) and supermicron ($d_p > 1$) components. Then the correlation between the trace element distribution and major element distributions were analyzed in two ways. First the cross correlation between the absolute concentration values on each relevant impactor stage was evaluated. Data from this correlation are summarized in Table 1 in the “Absolute Concentrations” columns for both submicron and supermicron regions.

A second method of assessing the possible correlation of trace elements to the cations is to evaluate the correlation between the differential distribution curves. This involved fitting a curve through the differential data in the region of interest and then plotting data derived from the trace element curve versus data derived from the major element curves (interpolating between the actual discrete data points on the differential distributions). An example of this method is illustrated in Figure 2. For the supermicron region, two 2nd order polynomials were fit through the five data points (Fig. 2a). Then the trace element curve is plotted against the major species curve (Fig. 2b) and the correlation is assessed. For the coal + MSS experiments, the polynomial through the data from the smaller diameter impactor stages represents the distribution in the near micron-sized fragmentation region while the data from the larger diameter impactor stages represents the distribution in the larger, bulk fly ash (the gas + MSS overall distribution does not indicate two separate particle regions). Each of these regions can be examined independently (Fig. 2c and 2d) for possible correlation. Results for all three trace elements are summarized in Table 1 under the “differential distributions” columns.

Submicron Correlation Results. The submicron region absolute concentration results suggest that the dominant partitioning mechanism is reaction with calcium for selenium and antimony during gas + MSS combustion. All other results in the submicron region are inconclusive. The differential distribution results suggest correlation between all three trace elements with calcium and/or iron in the gas + MSS experiments. Only antimony shows any correlation in the coal + MSS experiments – having a possible ($R^2 = 0.75$) correlation with calcium.

The differences in the “absolute concentrations” and “differential distribution” results are most likely due to the significant variation in absolute data from submicron impactor stage analysis. These stages typically have mass loadings an order of magnitude lower ($\text{Ø}[0.001\mu\text{g}]$ vs. $\text{Ø}[0.01\mu\text{g}]$). Therefore, gravimetric and analytical error imparts greater variability in the results from submicron stages than from supermicron stages. Thus, the differential correlation results are more likely to be indicative of correlation than the absolute value correlation in the submicron region.

Supramicron Correlation Results. The “absolute concentrations” results suggest that the dominant partitioning mechanism is reaction with calcium and/or iron for all three trace elements during gas + MSS combustion. For coal + MSS combustion, a similar conclusion is reached for arsenic and antimony but not for selenium.

The “differential distribution” results suggest possible correlation between the trace elements and both major elements for the gas + MSS experiments. It should be noted that the correlation between Sb and Ca or Fe is much weaker than As or Se correlation. Bulk fly ash region

correlation data suggests that all three trace elements are reactive with Ca and/or Fe but the fragmentation region data suggests reactivity only with Ca and not with Fe.

Previous research [7] has shown that none of these trace elements correlate with either calcium or iron during the combustion of the Ohio coal alone. The apparent correlation of these trace elements with calcium and/or iron in the “Coal + MSS” supermicron particle region results but not in submicron particle region suggests that calcium, and possibly iron, from the MSS becomes available for reaction on particle surfaces in the fragmentation and bulk particle size ranges. It should be noted that the fragmentation mode in the “Coal + MSS” PSD is less pronounced than for the “Coal only” PSD. This suggests that only the coal is participating in the fragmentation mechanism. Thus, the availability of calcium from MSS surface sites in this size range is most probably comparable to the availability in the bulk fly ash size range.

It is also revealing that there is an apparent lack of correlation between trace elements and iron in the fragmentation region when the bulk fly ash region results suggest correlation. Two possible explanations are 1) the trace elements are not actually reacting with iron but the similarity of the iron distribution to the calcium distribution results in an apparent correlation or 2) sulfur preferentially ties up iron surface sites in fragmentation sized-particles compared to bulk fly ash particles¹. The first of these alternatives is more likely since there is no apparent reason for preferential reactivity of sulfur with fragmentation iron surface sites compared to bulk surface sites.

To summarize, a detailed analysis of trace element vapor-to-solid phase partitioning suggests that reaction with calcium and iron surface sites is the controlling mechanism for MSS combustion with gas assist. For co-firing of Ohio coal with MSS, vapor-to-solid phase partitioning is controlled by the reaction with calcium in the supermicron region (due to active MSS-originating surface sites) but not in the submicron region.

FUTURE WORK

Future work will focus on fine particles and NO_x from staged combustion of coal/MSS mixtures.

¹ Previous research has shown that sulfur inhibits the reaction of arsenic with iron in high sulfur coals [7].

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TABLE 1
Correlation Coefficients for Trace Elements vs. Calcium, Iron, and Aluminum
in Fly Ash Particles from the MSS Experiments

		Supramicron Correlations					
		Submicron Correlations			Fragmentation		
Coal		Absolute Concentrations	Differential Distributions	Overall Absolute Concentrations	Overall Differential Distributions	Region Differential Distributions	Bulk Fly Ash Region Differential Distributions
ARSENIC CORRELATIONS							
Gas + MSS:	Ca	~0	~1	0.98	0.93	--	--
	Fe	0.47	~1	~1	0.93	--	--
Coal + MSS:	Ca	0.58	~0	0.87	0.93	0.96	~1
	Fe	~0	~0	0.92	~0	~0	~1
SELENIUM CORRELATIONS							
Gas + MSS:	Ca	0.83	~1	0.99	0.86	--	--
	Fe	~0	0.98	0.99	0.85	--	--
Coal + MSS:	Ca	0.63	~0	~0	~0	0.82	~1
	Fe	~0	~0	~0	0.56	~0	~1
ANTIMONY CORRELATIONS							
Gas + MSS:	Ca	0.90	0.98	0.99	0.71	--	--
	Fe	~0	~1	0.96	0.55	--	--
Coal + MSS:	Ca	0.49	0.75	0.87	~1	0.98	~1
	Fe	~0	~0	0.95	~0	~0	~1

Figure 1
Elemental Differential Distributions

FIGURE 2
CROSS CORRELATION OF DIFFERENTIAL DISTRIBUTIONS
ARSENIC vs. CALCIUM AND IRON IN
SUPERMICRON PARTICLE SIZE REGION
“COAL + MSS EXPERIMENTAL CONDITIONS”
a) Curve fitting the differential distributions
b) Total supermicron region correlation

(a)

(b)

FIGURE 2 (Continued)
CROSS CORRELATION OF DIFFERENTIAL DISTRIBUTIONS
ARSENIC vs. CALCIUM AND IRON IN
SUPERMICRON PARTICLE SIZE REGION
“COAL + MSS EXPERIMENTAL CONDITIONS”

c) Fragmentation region correlation

d) Bulk fly ash region correlation

(c)

(d)