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 Fourth Quarter of this project we present analysis of the data presented in previous quarterly reports. These data are on trace metal partitioning obtained from combustion of MSS and Gas, MSS and Coal and Coal and Gas alone. The results from coal plus municipal sewage sludge combustion suggest a particle size dependence for all three trace elements. This implies that the partitioning mechanism differs when co-firing MSS with coal than coal alone or MSS combusted with gas assist. The partitioning appears to be surface reaction or pore diffusion controlled.

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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 (Werther and Ogada, 1999). 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 Werther, and Ogada (1999).

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 (Hall, 1992). 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 (Werther and Ogada 1999). 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 (Cenni, et. al., 1998).

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

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. Some Figures of Report 4083R03 are repeated here for clarity.

Data characterizing the coal and MSS feedstocks are provided in the Second Quarterly Report 4083R02. Replicate experiments were performed with only natural gas ("Gas only"), MSS fired with natural gas assistance ("Gas + MSS"), only the Ohio 5/6/7 blend coal ("Coal only"), and MSS co-fired with the Ohio blend coal ("Coal + MSS"). Sample sets that most closely duplicated the typical ash mass particle size distribution were selected for elemental analysis. Arsenic, selenium, and antimony analyses were performed by graphite furnace atomic absorption spectroscopy (GFAA). Major species were analyzed by flame atomic absorption spectroscopy (AAS) or atomic emission spectroscopy (AES).

Differential elemental distributions for these key inorganic elements, developed following the method of Markowski and Ensor [5], are shown in Figure 1 for all four experimental conditions. The low concentrations of calcium and aluminum in the Ohio coal shown in Figure 1 are consistent with previous results for this coal [6]. Note the substantial increase in the submicron and vapor-phase concentrations of all major species when MSS is co-fired with coal compared to coal alone. The concentrations of major species in the vapor-phase and submicron regions is similar for the "Gas + MSS" and "Coal + MSS" profiles. This suggests that most of the material in these regions originated in the MSS feedstock. Natural gas is a significant feedstock source for As and Se but not for Sb. All three trace element profiles have a similar shape for the "Gas + MSS" results indicating similar partitioning mechanisms. The selenium profile for the "Coal + MSS" experiment is different from the arsenic and antimony profiles (which are similar). But in the "Coal only" experiment the As, Se, and Sb profiles are all similar. These results suggest that

there may be differences in the partitioning mechanisms of some of these trace elements when MSS is co-fired with coal compared to coal-only combustion.

Elemental Partitioning

The impact of co-firing on trace element partitioning can be further assessed by evaluating the net trace element differential distributions (Figure 2). To construct these curves, the trace element concentration ($\mu\text{g}/\text{Nm}^3$) on a given impactor stage for the baseline case ("Gas only" or "Coal only") was subtracted from the trace element concentration on the same impactor stage for the co-fired case ("Gas + MSS" or "Coal + MSS"). The net trace element concentration was then used to construct differential distributions following the method of Markowski and Ensor [5].

For the "MSS + Gas" test, there is a net increase in the concentration of all trace elements compared to the "Gas only" test. The smallest increases are for arsenic and antimony (where the concentration in the "Gas only" test is of the same order of magnitude as the concentration in the "MSS + Gas" test - the natural gas utilized in these tests has a fairly significant As and Sb content).

For the "Coal + MSS" test, there is a substantial increase in the trace elements in the bulk fly ash region. There is no appreciable difference in the vapor-phase and submicron phase concentrations. These results imply that there is no appreciable "scavenging" effect in co-firing MSS with this coal. In absolute terms, there is no substantial impact on trace element partitioning when MSS is co-fired with this Ohio coal.

Vapor-to-Solid Phase Partitioning Mechanisms

To determine the rate limiting mechanism, a number of researchers have analyzed partitioning behavior from the gas phase to particle surfaces using particle size dependence models based on transport theory [7-14]. For the supermicron particles, it can be shown that (assuming that the particles are spherical in shape and traveling at the same speed as the surrounding gas) transport of a trace element molecule from the vapor phase to the particle surface dominated by gas film transfer will follow an inverse dependence to the square of the particle diameter ($1/d_p^2$). Similarly, if transport is dominated by exterior surface reaction (assuming the particles are non-porous; a $1/d_p$ dependence may also indicate pore diffusion - controlled transport for porous particles), the distribution will follow an inverse dependence to the particle diameter ($1/d_p$) [15].

The supermicron region particle size dependence for the three trace elements studied at all four test conditions is shown in Figure 3. For the "Gas only" test, there is an apparent particle size dependence for the arsenic and selenium results ($1/d_p$). However, it should be noted that the total ash mass on these impactor stages is very low and these results may be an artifact of gravimetric measurement error [6].

Dependence ($1/d_p$) is indicated for arsenic and selenium in the "Gas + MSS" results. This suggests that surface reaction (or pore diffusion in porous particles) controls vapor-to-solid phase partitioning of these trace elements. For the "coal only" tests, no apparent particle size

dependence is observed. This result is consistent with previous results for this coal from more extensive testing [6]. These results suggest that the vapor-to-solid phase partitioning of these trace elements is not transport controlled.

The "Coal + MSS" results suggest a particle size dependence for all three trace elements. This implies that the partitioning mechanism differs when co-firing MSS with coal than coal alone or MSS combusted with gas assist. The partitioning appears to be surface reaction or pore diffusion controlled.

FUTURE WORK

Future work will attempt to correlate trace metals concentration and major species concentrations. Such major species are calcium, and silicon. This will provide insight into the nature of chemical reactions between trace metal vapors arising from MSS and other species.

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Figure 1
Elemental Differential Distributions

Figure 2

Net Trace Element Differential Distributions.

a) Net Trace Element Contribution from MSS during Gas Assist Combustion [(MSS + Gas) - Gas] and b) Net Trace Element Contribution from MSS during Coal co-firing [(MSS + Coal) - Coal]

Figure 3
Supermicron Region Particle Size Dependence for
Trace Elements from MSS Experiments