Particulate Emissions from Combustion of a Coal+Tire Blend

Reto Gieré 1, Huijun Li 2, Katherine Smith 2, and Mark Blackford 2

1 Universität Freiburg, Mineralogisch-Geochemisches Institut, Albertstrasse 23b, D-79104 Freiburg, Germany (giere@uni-freiburg.de); 2 Materials Division, ANSTO, Menai, NSW 2234, Australia

KEYWORDS: particulates, TDF, sulfates, zinc

ABSTRACT

The Purdue University power plant conducted an experiment with two different sets of fuel combusted at the same conditions: pure coal and a mixture of 95 wt% coal plus 5 wt% tire-derived fuel (TDF). A detailed chemical comparison was made of both types of fuel, the combustion products, and the atmospheric emissions. Compared to pure coal, the coal+TDF mixture is considerably richer in Zn, and also has a slightly higher S content. The increase in Zn is due to the high Zn content of the scrap tire chips. Emissions of Zn increased from 15 g/h to 2.4 kg/h when coal+TDF was combusted.

Particulate matter was collected on paper filters inserted into the top part of the smoke stack. It was characterized by scanning and transmission electron microscopy, and by electron microprobe. Amorphous material consists primarily of Al-Si-O glass spheres. Crystalline material comprises lime and mullite, and a variety of euhedral S-O phases (inferred to be sulfates), including sulfates of Ca, Pb, Fe (pure coal), and Zn (TDF+coal). The Fe- and Zn-sulfates range in size from a few nm to >100 µm. The large crystals must have formed only after the flue gas has passed through the air pollution control devices within the power plant. Detailed characterization of these particles is essential to assess the interaction between crystals and atmospheric moisture or rain, and thus the environmental impact of tire combustion.

INTRODUCTION

Accumulation of millions of scrap tires poses a considerable environmental problem. As an important part of the solid waste stream in today’s society, worn tires have traditionally been discarded in landfills or stored in stockpiles. Over the past several decades, however, innovative alternatives to disposal have been developed, partly as a result of high tipping fees charged by landfill operators. Because of their high heat content and their low levels of moisture and nitrogen compared to coal, tires are ideally suited for energy recovery through combustion. Utilization of waste tires as supplemental or alternate fuel in various industrial combustion facilities, thus, has become one of the most important alternatives to disposal.
Combustion processes, however, generate gaseous pollutants and solid waste materials, which must be disposed of or reused as secondary raw materials. It is therefore important to characterize these combustion products in order to assess the environmental impacts of energy recovery from scrap tires. Studies have shown that substantial reductions of some environmental pollutants can be achieved by partially replacing conventional fuels with waste tires. On the other hand, using tires as fuel may lead to considerable increases in the levels of other pollutants \(^1\). In this paper we will present results from the characterization of particulates emitted into the atmosphere during combustion of a coal+TDF mixture and compare them with those generated through combustion of pure coal.

EXPERIMENTAL SETUP

The Walter Wade Utility Plant provides the Purdue University campus (West Lafayette, IN) with heating steam, electricity and chilled water for air conditioning. There are four steam generators consisting of two spreader-stoker coal boilers, one oil/gas-fired unit, and one fluidized-bed coal boiler. The spreader-stoker boilers are equipped with cyclone-type mechanical collectors and electrostatic precipitators for air quality control (Fig. 1).

In 2001, Purdue University conducted an experiment with two different sets of fuel in successive weeks. During the first week, the power plant combusted pure coal, whereas a mixture of 95 wt% coal plus 5 wt% tire-derived fuel (TDF) was used as fuel during the second week. Combustion took place in a Detroit RotoGrate stoker boiler at ~1500 °C for both types of fuel. The TDF consisted of shredded tires, whereby the tire chips have a nominal size of 2.5 cm and contain some wires and synthetic fabric. The feed coal was sub-bituminous coal from Southern Indiana, consisting of similarly sized chunks \(^2\).

To collect escaped particulate matter (PM), filter papers were inserted into the top part of the smoke stack through sampling ports (Figs. 1, 2). The filters remained overnight in the smoke stack (about 12 hours) and trapped the fly ash fraction that was not retained by any of the air pollution control devices within the power plant. These particles would therefore have escaped into the atmosphere. They were trapped as a thin, black layer in all exposed areas of the round paper filters (Fig. 3). The particulate matter was then characterized by a variety of analytical instruments, including: a JEOL JSM 6400 scanning electron microscope (SEM) equipped with a Noran energy-dispersive X-ray spectrometer (EDS); a JEOL 2000 FXII transmission electron microscope (TEM) equipped with a Link ISIS EDS system, and a JEOL JXA-8900R electron probe microanalyzer (EPMA) equipped with three wavelength-dispersive crystal spectrometers and an EDS system. Additional analytical techniques used for characterization included X-ray diffraction and micro-Raman spectroscopy.
Figure 1. Schematic diagram of a stoker-boiler unit at Wade Utility Plant of Purdue University. Sampling points are shown in blue and include those for collection of stack ash (SA) on filter paper inserted into the smoke stack (this material consists of PM); electrostatic precipitator ash (PA); mechanical separator ash (MA); and bottom ash (BA). Other symbols and numbers indicate the following: forced draft fan (FDF); induced draft fan (IDF); outside air heater (1); steam reheater (2); Ljungstrom rotary air heater (3); manual hoppers (4); mechanical cyclone separator hoppers (5); electrostatic precipitator hoppers (6). Green arrows show inlet air flow, red arrows show outlet air flow.
RESULTS

A detailed chemical comparison was made of both types of fuel, the solid combustion products (bottom ash, mechanical collector ash, electrostatic precipitator ash), and the atmospheric emissions. Compared to pure coal, the coal+TDF mixture is considerably richer in Zn (183±42 vs. 36±16 ppm), and also has a marginally higher S content (2.0±0.4 vs. 1.5±0.2 wt%). The increase in Zn is due to the high Zn content of the scrap tire chips (~1.1 wt%). Most of the other 59 elements studied have similar concentrations in both types of fuel. Analogous observations were also made for the solid waste materials. For example, the Zn contents of electrostatic precipitator ash resulting from coal and coal+TDF combustion are ~3500 ppm and ~56,000 ppm, respectively.

The Purdue University experiment documents that combustion of the coal+TDF blend rather than pure coal leads to significantly enhanced average emissions of various metals and metalloids, including Be, Al, Cr, Ni, Cu, Zn, As, Cd, Sb, and Pb. Most dramatic are the increases observed for Zn, whose emissions averaged nearly 2.4 kg/h for the coal+TDF blend, compared to 15 g/h for the combustion of pure coal. On the other hand, emissions of Hg and total PM remained constant. These results are similar to those of another study, performed at the University of Iowa.

To characterize better these metal emissions, the chemical and structural properties of the particulates trapped on the filter papers have been investigated. The examination by SEM of the filter papers revealed that the trapped material consists mainly of very fine particles. These particles, typically <1 μm across, occur as aggregates and form a thin layer on the filter paper (Fig. 4). In an attempt to obtain bulk compositional information about this PM layer, three areas of ~20 μm² were rastered with a focused electron beam. The bulk chemical data obtained by this technique (Table 1) are semi-
Figure 4. SEM pictures showing the layer of particulate material deposited on the filter paper at small (left) and larger (right) magnification.

Table 1. SEM-EDS analyses (in wt%) from 20 µm square areas of the PM layer deposited on the filter papers. These analyses are semi-quantitative at best and give an indication of the bulk composition of the emitted PM.

<table>
<thead>
<tr>
<th></th>
<th>PM derived from coal</th>
<th>PM derived from Coal+TDF</th>
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<tbody>
<tr>
<td></td>
<td>1  2  3   Average  Std dev</td>
<td>1  2  3  Average  Std dev</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.7  1.9  1.3  1.6  0.3</td>
<td>6.1  0.7  6.5  6.4  0.3</td>
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<tr>
<td>Na₂O</td>
<td>0.2  0.5  0.6  0.4  0.2</td>
<td>1.6  2.6  2.3  2.2  0.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.3  0.4  0.9  0.5  0.3</td>
<td>1.8  0.3  2.2  1  1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.2 13.1 11.4 14  2</td>
<td>6.0  19.1 5.1  10  8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.0 31.1 29.1 31  2</td>
<td>13.0 39.5 6.9  20  17</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.8  1.3  1.6  1.6  0.3</td>
<td>26.4  2.8  30.8  20  15</td>
</tr>
<tr>
<td>SO₂</td>
<td>29.1 29.2 33.0 30  2</td>
<td>19.9 19.2 20.1 19.7 0.5</td>
</tr>
<tr>
<td>FeO</td>
<td>9.7  12.0 10.2 11  1</td>
<td>2.8  4.2  3.0  3.3  0.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.2  0.8  1.3  0.8  0.6</td>
<td>5.7  6.3  6.1  6.0  0.3</td>
</tr>
<tr>
<td>CuO</td>
<td>1.8  2.1  1.6  1.8  0.3</td>
<td>1.7  1.6  1.1  1.5  0.3</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.2  n.d.  n.d.  0.2</td>
<td>0.3  0.2  0.2  0.2  0.1</td>
</tr>
<tr>
<td>NiO</td>
<td>0.3  0.7  0.4  0.5  0.2</td>
<td>0.1  0.1  n.d.  0.1</td>
</tr>
<tr>
<td>GeO₂</td>
<td>1.7  2.8  2.4  2.3  0.6</td>
<td>13.3  0.9  13.9  9  7</td>
</tr>
</tbody>
</table>
quantitative at best, because the SEM was calibrated for EDS point analysis. The data show considerable variation and, consequently, the standard deviations of the average values are substantial. Especially large are the variations in the concentration of Si, P, Ti, and Ge in the PM derived from combustion of coal+TDF. The chemical data reveal, however, that the trapped PM derived from coal+TDF combustion is substantially richer in Zn, but contains less Fe and S than that derived from pure coal. The high Ge contents observed in the PM are due to the rather high Ge content of Indiana coal 4.

The PM layer on the filter papers supports a multitude of larger particles, including:

a) pieces of unburnt carbon (Figs. 5, 6)

b) aluminum-silicate spheres with diameters of up to ~100 µm (Fig. 7). These spheres, some of which are cenospheres, may have S-rich phases attached to their surfaces or contain substantial amounts of S either within or on their surface. The spheres are very similar to those typical of most fly ashes generated through coal combustion 5,6.

c) aluminum-sulfate needles, which are probably crystalline and may be >200 µm long (Fig. 8). Some of these needles occur in clusters, are whisker-like in shape, and additionally contain considerable amounts of Mg (Fig. 9).

d) large (commonly >100 µm across), euhedral crystals of S- and O-rich phases, presumably sulfates (Fig. 10, 11, 12). These crystals are typically twinned and often occur as clusters. When pure coal was combusted, they contain as major components S, O, Fe, Mg and K (Fig. 10). When the coal+TDF blend was combusted, these sulfate crystals contain Zn as predominant base metal (Fig. 11).

Figure 5. SEM picture of a large carbon piece supported by the PM layer on the filter paper (pure coal).

Figure 6. Large-magnification SEM picture showing details of a large carbon piece on the filter paper (pure coal).
Figure 7. SEM picture (top) and EDS spectrum (bottom) of an aluminosilicate sphere supported by a thin layer of PM deposited on the filter paper (pure coal). In addition to Al, Si, and O, the sphere contains substantial amounts of Mg, S, K, and Fe as well as minor amounts of Na, P, Ca, and Ti. The crystals attached to the surface of the sphere are Fe-, S- and O-rich phases (probably Fe-sulfates). The C peak is from the coating.
Figure 8. SEM picture (left) and EDS spectrum (right) of an Al-, S-, and O-rich needle, presumably an Al-sulfate, supported by a thin layer of PM deposited on the filter paper (pure coal). The needle also contains some Si. The C peak results from the coating.

Figure 9. SEM picture (left) and EDS spectrum (right) of a cluster of Al-, S-, and O-rich needles, presumably Al-sulfates, supported by a thin layer of PM deposited on the filter paper (pure coal). These whisker-like needles contain also substantial amounts of Mg. The C peak results from the coating.
Figure 10. SEM picture (top) and EDS spectrum (bottom) of clusters of twinned, euhedral Fe-, S-, and O-rich crystals, presumably Fe-sulfates, supported by a thin layer of PM deposited on the filter paper (pure coal). The crystals contain additionally substantial amounts of Mg, Al, P, and K. The C peak results from the coating.
Figure 11. SEM picture (top) and EDS spectrum (bottom) of clusters of twinned, euhedral Zn-, Fe-, S-, and O-rich crystals, presumably Fe-rich Zn-sulfates, supported by a thin layer of PM deposited on the filter paper (coal+TDF). The crystals contain additionally considerable amounts of Mg, Al, P, and K. The C peak results from the coating. The fibers visible in the SEM image are the filter paper.
Figure 12. Large-magnification SEM picture of clusters of twinned, euhedral Zn-, Fe-, S-, and O-rich crystals on the filter paper (coal+TDF). These crystals are very similar in composition to those shown in Figure 11.

DISCUSSION

Preliminary TEM investigations have shown that the particulates comprise amorphous and crystalline material, and are similar for both types of fuel. The amorphous material consists primarily of Al-Si-O spheres, similar to those observed in fly ash from coal combustion. In addition to the crystalline phases observed by SEM, the following
crystalline particles were identified by TEM: lime (CaO), mullite (ideally Al₆Si₂O₁₃), Ca-sulfate, and Pb-sulfate.

The large crystals must have been formed only after the flue gas has passed through the air pollution control devices within the power plant. We conclude that these crystals represent condensates, which precipitated from the flue gases. Most likely, deposition on the filter papers was induced by the presence of PM, which acted as substrate for nucleation. We are in the process of characterizing the structure and chemical composition of these crystals as well as all PM using TEM, EPMA and micro-Raman techniques. Detailed characterization of these particles is essential to assess the interaction between crystals and atmospheric moisture or rain, and thus the environmental impact of tire combustion.

REFERENCES


