Morphology and composition of the fly ash particles produced in incineration of municipal solid waste

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Received 1 March 2001; received in revised form 1 October 2001; accepted 1 December 2001

Abstract

This paper describes the results of experiments using a pilot-scale, 140,000 Btu/h, solid fuel continuous feed laboratory incinerator. A synthetic fuel representative of the municipal solid waste in the United States was formulated and used in this research. The fuel contained Fe and SiO₂, and was doped with trace amounts of Al, Ni, Cr, Hg, and PbO. Experiments were performed with varying fuel–air ratio, and both gaseous and condensed products were collected and analyzed. This work focuses on the characterization of composition and morphology of fly ash particles captured in a fabric filter. Particle size distributions were obtained using optical microscopy and sieving. Atomic absorption (AA) was used to determine bulk compositions of the size-classified ash fractions. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were used to study the morphology and surface compositions of the ash particles. It was observed that the fly ash particles have bimodal size distribution and, most interestingly, that the ash particles of different sizes have different elemental and phase compositions. Concentrations of Cr, Ni, and Fe were greater in the coarse particles (up to 1-mm diameter), whereas concentrations of Al and Si were higher in the finer particles (less than 75 μm). Maximum concentrations of Pb and Hg occurred in the 150–300-μm particles. It is suggested that if a correlation between the composition and size of the ash particles similar to that observed in this research exists in the products of industrial combustors, a technique of ash processing based on the particle size classification could be developed. Applying such a technique could result in the efficient and inexpensive removal of the lead- and mercury-rich particulates from the produced ash. The processed, environmentally benign ash portions will therefore be useful for a variety of the recycling-based manufacturing, and metal recovery processes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Morphology and composition; Fly ash particles; Incineration

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1. Introduction

Toxic, metallic trace elements contained in coal and refuse-derived fuels present a serious environmental problem that has stimulated a wide range of research efforts (e.g., see Refs. [1–3]). Most studies have focused on capturing the hazardous metal-containing particulates that escape current filters (e.g., 0.11 μm and nanosized particles). Fewer studies have addressed the issue of the phases and morphology of the ash that is collected and is known to be saturated with many metal species, many of them are often bonded to carbon [4]. The bonding mechanisms and strength are not well known. Thus, in most cases, to avoid the contamination of soil and groundwater, toxic metals should be removed before the ash is buried in the landfills or used in manufacturing of cements or other commodity materials. Information on metal speciation, phase compositions, and morphology of the ash particles is needed to efficiently separate the toxic species from the collected ash. In the past, significant efforts have been applied to characterize the partitioning of trace metals in the ash [1,3]; however, only total atomic fractions of metals have been reported in most cases. Researchers did not specify chemical compositions and morphology of the ash metal phases even though such information is crucial for the development of adequate technologies for removal, neutralization, or recycling of the toxic metal species.

The lack of information on the chemical composition and morphology of the produced ash particles is largely due to experimental difficulties in gathering representative data using ash samples from large-scale industrial combustors. At the same time, the complex heat and mass transfer processes occurring in different sections of large-scale installations with continuous fuel feed systems and including primary and secondary combustion chambers, staged heat exchangers, and electrostatic or fabric filters determine the mechanisms of ash formation. These mechanisms depend on the temperature changes and two-phase flow patterns existing in different parts of industrial scale combustors and cannot be adequately imitated in well-instrumented bench-scale burners.

Recently, a unique 140,000 Btu/h pilot-scale laboratory combustor has been developed at NJIT with the primary goal of studying the mechanisms governing combustion of municipal waste and refuse-derived fuels [5]. A schematic diagram of the apparatus is shown in Fig. 1. It is a continuous solid fuel feed facility with an automatically moving fuel grate and capabilities to control independently the underfire and the overfire air flows, and adjust the temperatures in the primary and secondary combustion chambers. It is equipped with various diagnostics, e.g., thermocouples, gas sampling ports for in situ gas chromatography, and windows for optical observations and measurements. In a recent study exploiting this facility, a synthetic fuel representative of the municipal solid waste in the United States was formulated and produced in 600-lb batches [6]. The main dry components of the synthetic fuel are described in Table 1. These components were mixed and shredded in a small hammer-mill shredder (12-in. flakebreaker by Jacobson). The shredder reduced the size of paper, mulch, and animal feed to a fluffy mixture of particles of less than 1-mm size. To imitate the moisture content of MSW, 20 wt.% of water was added to the fluff before compaction. The fuel was also doped with trace amounts of Al, Ni, Cr (99% pure metal powders), 99.999 pure liquid Hg, and PbO powder, all from Fisher Chemical. The mixture was then compacted into cylindrical pellets of 2.5-cm diameter and average 5-cm length using a HYFLO California Pellet Mill. The selected size of the pellets corresponded to their
volatilization times of about 20 min, close to the experimental residence time of MSW in the primary combustion chamber of commercial incinerators [3].

Experiments were conducted on combustion of the synthetic fuel in the pilot-scale incinerator with varying fuel–air ratio. Both gaseous and condensed combustion products were sampled and analyzed. The total amounts of metals in different components of combustion products were determined using atomic absorption (AA) spectroscopy. The phases of main metal components in fly and bottom ash were determined using X-ray diffraction (XRD) and compared with the product compositions expected from predictions based on thermodynamic equilibrium [6,7]. A number of metal-containing species were found in both bottom and fly ashes that have not been predicted as products by the equilibrium estimates. It has been also observed that the captured fly ash particles are characterized by an extremely wide particle size distribution, and it was hypothesized that

Table 1
Dry components of the synthetic fuel imitating MSW

<table>
<thead>
<tr>
<th>MSW component</th>
<th>Representative synthetic fuel component</th>
<th>Mass (%)</th>
<th>Particle size, morphology</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper and paperbound wood</td>
<td>Newsprint paper</td>
<td>35</td>
<td>3–5-in. strips</td>
<td>Ink-free, by Vanguard Offset Printers, Hillside, NJ</td>
</tr>
<tr>
<td>Yard trimming, wood</td>
<td>Hardwood mulch</td>
<td>17</td>
<td>2–3-mm particles</td>
<td>Pecquanock lumber mill, NJ</td>
</tr>
<tr>
<td>Plastics</td>
<td>Low density polyethylene</td>
<td>14</td>
<td>0.5-mm granules</td>
<td>98% pure, by Chevron Polyethylene Resins</td>
</tr>
<tr>
<td>Metals</td>
<td>Iron</td>
<td>8</td>
<td>0.2–0.5-mm iron filings</td>
<td>99% pure, by Fisher Chemicals</td>
</tr>
<tr>
<td>Food wastes</td>
<td>Animal feed</td>
<td>5</td>
<td>Recreational horse food</td>
<td>Agway</td>
</tr>
<tr>
<td>Glass</td>
<td>Sand</td>
<td>1</td>
<td>Particles less than 0.2 mm</td>
<td>A construction supplier, NJ</td>
</tr>
</tbody>
</table>
different mechanisms could be significant in the formation of different size particles. In addition, it was expected that if significant difference in the chemical composition is found for the particles of different sizes, an ash processing technique based on size classification could be developed to remove most of the toxic species from the ash prior to its recycling or burying in the landfills.

This research was aimed to test the above hypotheses and characterize the morphology, phases, and compositions of the produced fly ash particles of different sizes.

2. Combustion experiments and overall fly ash composition

Nine combustion experiments have been conducted with the equivalence ratio varied around 0.2–0.3 to imitate the lean conditions normally used in practical incinerators [2]. A pilot natural gas-air flame was used to ignite the solid fuel. A steady state combustion regime was established after about 1 h. The temperature in the primary combustion chamber was continuously monitored using an internally mounted thermocouple. The thermocouple was placed in the top portion of the chamber and showed a temperature variation from 830 to 860 °C with different fuel–air ratios. In addition, a digital video camera and three-color pyrometer set-up at a window in the primary combustion chamber were used to monitor the flame radiation and temperature distribution in the region close to the center of the chamber. The optical measurements indicated that the temperature at the center of the primary combustion chamber was not uniform and varied from 880 to 950 °C. However, once a steady state combustion regime was established, the average temperature and the range of the temperature variation remained constant.

Normally, one batch of synthetic fuel was used in three consecutive experiments. The duration of each experiment was in the range of 6 to 8 h. The overall ash composition and metal partitioning between the fly ash, bottom ash, and the flue gas were studied using atomic absorption measurements and X-ray diffraction, as described in Ref. [7]. Fly ash samples were recovered after each experiment from the “bag-house” fabric filter.

Metals contents in the fly ash were determined using atomic absorption measurements; carbon, chlorine, hydrogen, nitrogen, and sulfur contents were obtained using standard
ASTM chemical tests [8]. The remaining mass balance was assumed to be oxygen. The resulting overall composition for the fly ash is shown in Fig. 2. In addition to the main elements, C, Fe, H, N, S, Cl, O, and Si, the ash percentage composed of the trace metals (Al, Ni, Cr, Pb, and Hg) is lumped together and shown as the overall trace metal content labeled M.

3. Fly ash particle size distribution and density

The particle size distribution was obtained using optical microscopy. The fly ash samples were dispersed in oil on surfaces of microscope glass slides. A microscope was coupled to a video camera and a Snappy board was used to digitize the images for further processing. These images were processed using a UTHSCSA Imagetool software. The image processing included subtraction of background (an image acquired with no particles on the slide but with the same field illumination) to produce a uniform initial image brightness, Gaussian filtering, and boost of contrast. Each particle on the image, identified by the software as an object, was converted into a perfect circle with the same area as the original particle. The diameter of such a circle, called “Feret diameter”, was measured for each object automatically so that the particle size distribution was determined. Each image included 50–100 particles, and at least 10 images were collected and processed for each ash sample to provide an acceptable quality size distribution. An example of the representative size distribution for fly ash particles is shown in Fig. 3. Such bimodal size distributions were consistently observed for ash samples collected after different combustion runs. The measured size distribution covers a very wide particle size range, so that some of the details, e.g., the size distribution in the range of 0–75 \( \mu \text{m} \), have not been resolved. The presence of very coarse particles, greater than 500 \( \mu \text{m} \), in the fly ash was not expected.

In addition to the microscopic measurements, the fly ash particles were size-classified using a set of four sieves with the 75-, 150-, 300- and 1000-\( \mu \text{m} \) opening sizes. A sieve shaker was used and the size classification was complete during 1 h. The masses of each of the

Fig. 3. Size distribution of the fly ash particles determined using optical microscopy.
separated fractions of the fly ash particles were determined. As shown in Fig. 4, the results of these measurements are in qualitative agreement with the size distribution determined using optical microscopy. A more detailed comparison of the fly ash particle size distributions determined by optical microscopy (Fig. 3) and sieving (Fig. 4) indicates that the larger particles represent a greater mass fraction according to the optical microscopy. An explanation of this discrepancy could be that sieving causes break-up of some of the loosely agglomerated particles that are counted as single particles by the optical image processing software.

![Fig. 4. Size distribution of the fly ash particles determined using sieving.](image)

![Fig. 5. Densities of different size fractions of fly ash.](image)
The densities of the different size fractions of the fly ash particles were determined using a 10-ml glass picnometer. The results of these measurements are shown in Fig. 5.

4. Morphology and compositions of different size fly ash particles

The compositions of the different size fractions of fly ash particles were determined using atomic absorption (AA) measurements. The fly ash samples were dissolved in nitric acid and a flame AA instrument by Thermo Jarrell Ash was used for the analysis. The measurements have been conducted for six ash samples collected after different incinerator runs. It was observed that the concentrations of metal species were different for different size fractions of the fly ash particles. The trends observed for the changes in composition as a function of particle size were repeatable from sample to sample and are illustrated in Fig. 6. The results of measurements were normalized within each size fraction but not over the bulk fly ash composition. Therefore, the sum of each metal’s percentage presented in Fig. 6 for each size fraction will result in 100%. This form of presentation was chosen to better illustrate similar trends and relative changes in metals concentrations as a function of the particle size. The total absolute mass percentages of different metals in the bulk fly ash are given in the caption of Fig. 6. The amounts of Cr, Ni, and Fe in the particles are

![Diagram showing metal mass percentages per fly ash size fraction](image)

Fig. 6. Atomic absorption results on elemental compositions of different size fractions of the fly ash particles. The total metal mass concentrations in the fly ash are: Cr — 0.025%; Al — 0.12%; Ni — 0.028%; Fe — 13.35%; Si — 2.11%; Hg — 0.069%; Pb — 0.030%).
increasing as the particle size increases, while the opposite trend is observed for Al and Si. The intermediate size particles are observed to contain the most significant amounts of the volatile metals, Pb and Hg.

X-ray diffraction (XRD) was used to determine the phase compositions of the fly ash particles of different sizes. The samples for the analyses were prepared using the size-classified ash. Before XRD patterns were collected, all samples were examined visually under an optical microscope (≈ 40 × magnification). Within coarse fractions (> 150 μm), grains of magnetite, Fe₃O₄, and unaltered iron were clearly visible, as were quartz grains that were frequently coated with a thin black layer. All samples were strongly magnetic. Iron hydroxides FeOOH were present in all samples as irregularly shaped lumps, coating on larger Fe/magnetite grains, or small spherules. Carbon black was present in all fractions except larger than 1 mm, and its relative amount increased noticeably with decreasing particle size. All fractions except the largest had a “waxy feel,” indicating the presence of organic components other than pure carbon. None of the fractions showed any effervescence when exposed to HCl, therefore carbonates are unlikely to be present in substantial quantities.

The coarse fly ash particles were not well suited for the X-ray diffraction analysis for which fine powder samples are normally used. Therefore, size-classified ash samples were ground for less than 10 min in a high energy ball mill SPEX 8000. As a result, sized particles were reduced to several microns.

Diffraction patterns were collected on a Philips X’Pert diffractometer using Cu Kα radiation (λ = 1.5418 Å). No monochromator was used. Patterns were collected as continuous scans between 15° and 70° 2θ with an increment of 0.03° and 15 s counting time. Due to the relatively high iron content of the samples, the Cu radiation caused significant fluorescence, thereby polluting the collected patterns. Parameters for pulse height discrimination of the detector system were adjusted to minimize this effect, but the overall signal to noise ratio was still significantly higher than usually seen for iron-free samples. Results of the measurements are illustrated in Fig. 7; in addition to the measurements for the size-classified ash fractions, an X-ray diffraction pattern collected for the unburnt fuel used in the experiments is shown for reference.

To identify phases present in the ash samples, peak positions were determined manually, using minima in the second derivatives of the diffraction traces as guides. These peak positions were checked against the JCPDS Powder Diffraction File [9]. The following major components were identified unambiguously:

FeOOH, akaganeite (JCPDS #34-1266)
Fe₂O₃, hematite (JCPDS #33-664)
Fe₃O₄, magnetite (JCPDS #19-629)
Fe, α-iron (JCPDS #6-696)
SiO₂, quartz (JCPDS #46-1045)
SiO₂, cristobalite (JCPDS #39-1425)

Fe₃O₄ magnetite and unaltered metallic iron appear in all size fractions. Fe₂O₃ was only present in the largest size fraction (>1 mm) in significant quantities. All remaining fractions contained the hydroxide, FeOOH. The iron detected in the finer ash fractions could be the
result of vaporization and reduction of iron oxide formed in the primary combustion chamber [3].

The presence of SiO₂ was most significant in the largest and in the two smallest fractions (< 75 and 75–150 μm). While the largest fraction showed only quartz, which was a fuel component, the finer fractions, in addition, showed cristobalite, probably formed as high-temperature condensation product.

The two smallest fractions showed a raised background between about 20° and 40° compared to the coarser fractions, indicating increasing amount of amorphous or cryptocrystalline components. A number of diffraction lines in the finer fractions could not be unambiguously identified. Phases that are potential candidates include: CaSO₄·2H₂O, gypsum (JCPDS #33-311); NaCl, halite (JCPDS #5-628); Al₂O₃, δ-alumina (JCPDS #4-877); SiCl₄, (JCPDS #10-220); Ca₃Fe₂O₅, srebrodolskite (JCPDS #47-1744). The presence of poorly crystalline aluminosilicates is also likely and would be consistent with the atomic absorption measurements showing increase in Al and Si contents in the finer ash particles. For future work, a number of additional methods should be employed parallel to X-ray diffraction to identify the above phases unambiguously. These methods include chemical pretreatment of the ashes to separate components soluble in water, acids or organic solvents, magnetic separation of iron and iron oxides, determination of ignition weight loss at various temperatures (TGA), removal of organic and/or volatile components by high-temperature treatment (>1500 °C), and systematic optical microscopy.

The measurements described above and producing the information on the bulk compositions and phases of different size ash particles have been in qualitative agreement with the elemental composition measurements for individual particles. An Electro Scan environmental scanning electron microscope (SEM) integrated with Kevex Sigma 3 energy dispersive X-ray spectroscopy detector (EDS) was used to study morphology and identify
compositions of individual fly ash particles. The results of these analyses are illustrated in Figs. 8 and 9. While great variety of particle shapes and compositions were observed within each analyzed sample, based on the reviewing of a number of particle images, it became possible to identify particle types or morphologies specific for each size range. Thus, the particle images and compositions discussed below represent particles uniquely found in specific size ranges. A typical image of a large particle found in the fly ash is shown in Fig. 8a. It can be noted that the core of the particle is monolithic, and thus the large particles found in the fly ash are not agglomerates of smaller particles. Indications of the layered surface morphology are visible, also smaller particles are attached to the large, monolithic particle surface. The EDS spectra shown in Fig. 8 indicate strong peaks of iron (both $K_{\alpha}$ and $K_{\beta}$), in agreement with the AA and XRD measurements. In addition, $K_{\alpha}$ peaks of both Ni and Cr are clearly visible for this particle’s spectrum. Note that the sensitivity of the EDS
measurements is very high for the metals and heavier elements, so that they are readily detected even though their relative contents could be too low to be detected by XRD. Peaks of oxygen (K\textsubscript{α}) and chlorine (K\textsubscript{α}) are also evident in the EDS spectra for this and all other particles.

An image of a typical fly ash particle of the size in the range of 150–300 μm is shown in Fig. 8b. The particle has a crystalline core and a large number of smaller, 10–30 μm, particles are attached to its surface. The bond between the crystalline core and the attached particles is expected to be reasonably strong because the small particles remained attached in spite of the processing of the fly ash in the sieve shaker. As shown in the EDS spectrum for this particle (cf. Fig. 9), iron peaks disappear, but strong Hg and Pb peaks appear indicative of the high content of these two volatile and toxic metals in the particles of this size range. As shown in Figs. 3 and 4, the number of fly ash particles in this size range is relatively small, but, as shown in Fig. 5, they contain the greatest amounts of lead and mercury. It is, therefore, suggested that size classification of particles of this size fraction could significantly reduce amounts of these toxic metals in the reminder of the fly ash.

A typical image of a particle from the size range of 75–150 μm is shown in Fig. 8c. The particle core consists of different size rectangular crystallites. In addition, a number of micron-size spherical particles can be found attached to the particle surface. A strong aluminum peak appears in the EDS spectrum measured for this particle, as shown in Fig. 9.

Finally, an image of a 25-μm size particle is shown in Fig. 8d. It is a crystalline particle with porous structure, no smaller particles can be seen attached to it. Strong Al and Si
peaks are observed at the EDS spectrum (Fig. 8) measured for this particle, in agreement with the AA measurements showing the highest Al and Si contents in the particles of less than 75-μm size.

5. Concluding remarks

The nature of the observed difference in the compositions of the different size fly ash particles is not immediately clear. It is suggested that the comparison of the oxidation and volatilization rates of different species with their feed rate into the combustion chamber might indicate the mechanisms responsible for the observed trends. Sampling of the fly ash from different locations of the incinerator is also suggested to be useful. While additional research is needed to better understand the processes leading to the partitioning of metal species between the fly ash particles of different sizes, the practical implications of the reported here experimental results could be exploited almost immediately. For example, an inexpensive and straightforward technique of ash processing based on the particle size classification could be developed. Applying such a technique could result in the efficient removal of the lead- and mercury-rich particulates from the produced ash. The processed, environmentally benign ash portions will therefore be useful for a variety of the recycling-based manufacturing technologies. At the same time, mercury and lead can be recovered from the separated ash fractions rich with these metals and used in the manufacturing employing mercury and lead. Other materials, e.g., iron, iron oxides, and silica, could also be recovered more effectively if the collected fly ash is preliminary size-classified.

In order to start development of new ash processing technologies, it would be important to find out how similar or dissimilar the compositions of the different size ash particles are when the ash samples are produced in different combustors. It would also be interesting to determine whether the trends in the morphology and composition found for the ash of synthetic fuel imitating solid waste are also valid for coal-based fuels.

References