Metal partitioning in products of incineration of municipal solid waste

Sukrut S. Thipse, Edward L. Dreizin*

Department of Mechanical Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102-1982, USA

Received 1 March 2001; received in revised form 13 June 2001; accepted 13 June 2001

Abstract

Metals contained in the waste transfer to the waste incineration products, including flue gas, fly ash, and bottom ash, as different oxide, nitride, carbides, and other phases. Most of the metal-based phases formed in incineration are toxic and their emissions need to be strictly controlled. Therefore, behavior of metal species during incineration must be well understood. Such understanding is possible based on the experimental identification of the metal phases formed in the waste combustion and determination of their concentration in various incineration products. To avoid well-known experimental difficulties of the industrial waste incinerators associated with the poor fuel/conditions reproducibility and limited instrumentation, a 140,000 Btu/h pilot-scale, laboratory burner was constructed, characterized and operated at NJIT. A synthetic fuel representative of the municipal solid waste in the US was formulated and produced in 600-Lb batches. The solid fuel contained Fe and SiO2 as main constituents, and was doped with trace amounts of Al, Ni, Cr, Hg and PbO. Several experiments have been conducted on combustion of the synthetic fuel in the pilot-scale incinerator with varying fuel–air equivalence ratio. Both gaseous and condensed combustion products were sampled and analyzed. Atomic absorption spectroscopy and X-ray diffraction were used to analyze total metal contents and metal containing phases in the incineration products. Thermodynamic equilibrium computations were performed to obtain the adiabatic flame temperature and identify the phases of the metal-containing products formed at the equilibrium conditions. The results of the equilibrium computations performed at the varied fuel/air ratios were compared with the observed experimental results. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Municipal solid waste; Metal partitioning; Atomic absorption spectroscopy; X-ray diffraction

1. Introduction

Research on the mechanisms of metal partitioning in the products of waste incinerators has been active (e.g., Wu and Biswas, 1993; Linak and Wendt, 1993) due to the toxicity of many metal species found in the incineration products. Most of the relevant experimental efforts have addressed the operation of industrial incinerators (Niessen, 1995). However, the results of such studies are hard to reproduce and interpret in terms of the mechanistic understanding of the metal partitioning processes. Metal partitioning in waste incineration has also been studied using laboratory scale burners and incinerator models (Linak and Wendt, 1993; Karimanal and Hall, 1996), which are much better instrumented, but only partially imitate the conditions and processes occurring in industrial facilities.

Most of the reported results specify amounts of different metals in the incineration products in terms of elemental metal mass or atomic fractions (e.g., Reimann, 1989; Nakamura et al., 1996; Binner et al., 1997). Such information is valuable, but often is not sufficient...
for the adequate processing of the incineration products. Specifically, the behavior of metals in the ground-fills and in the materials made using the incineration ash (e.g., cement) depends on the types of the metal species present in the ash and on the morphology of the metal-containing particles. Even though the number of relevant studies has become significant, identification of the metal phases and morphology of the metal-containing particles in the incineration products is still lacking. Partially, the lack of this information is due to the extreme complexity of the processes occurring in a practical incinerator and difficulties in the producing the laboratory imitations or models of such processes.

In order to adequately characterize different metal phases formed in the incineration products, a well-instrumented, continuous feed, pilot scale 140,000 Btu/h (41 kW) incinerator facility has been recently developed (Thipse et al., 1999, 2001). In addition, a well-characterized and reproducible synthetic fuel has been developed that closely imitates municipal solid waste (MSW) (Thipse et al., 2001). Therefore, laboratory experimental studies of processes, mechanisms, and products of waste incineration could be conducted that would represent industrial incineration technologies much better than was possible in the past.

The objective of this research is to exploit the new facility and classify and characterize various types of metal phases produced in the incineration products and their distribution between the generated bottom ash and fly ash. The results of this work and their implications are discussed below and compared with some of the available information on metals partitioning in municipal solid waste incineration.

2. Technical approach

2.1. Experimental setup

Both incinerator design and synthetic fuel composition and parameters have been described elsewhere (Thipse et al., 1999; Thipse et al., 2001) and only a brief overview is given below. A simplified schematic diagram of the NJIT laboratory incinerator is shown in Fig. 1. It includes two (primary and secondary) combustion chambers, heat exchangers, and filters. The 0.11 m³ primary combustion chamber has a moving grate to maintain the fuel mixing. Fuel is fed at a rate of 10–13 kg/h and its residence time on the grate ranges from 20 to 30 min. Both underfire and overfire airflows (combined flow rate of 64–81 cfm) are introduced to the chamber and are independently controlled. The volatilization products pass into the secondary combustion chamber, a vertical pipe that is thermally insulated both inside and outside to prevent heat losses. The flue gas residence time in the secondary chamber is in the order of 1–2 s. A continuous gas emissions monitoring system determines the concentrations of O₂, CO, and NO at the exit of the secondary combustion chamber. The two-step heat exchanger is used to cool the flue gases, and a fabric filter bag-house collects the fly ash. An induced draft exhaust fan provides a continuous gas flow through the incinerator system. Steady-state temperature regimes were achieved and reproduced when the same fuel feed rates and airflow rates were used.

2.2. Synthetic fuel

The synthetic fuel has been produced based on the composition of municipal solid waste traced over the years by the US Environmental Protection Agency (EPA) (USEPA, 1996). The MSW composition and the synthetic fuel composition are shown in Table 1. A series of sequential tests developed by ASTM for the refuse-derived fuels (ASTM, 1996) was conducted to determine moisture, volatile matter, fixed carbon and ash contents of the synthetic fuels. These tests showed that the synthetic fuel imitates the MSW reasonably well. An ASTM test series was repeated for each prepared fuel batch. The comparison of the test results for different fuel batches confirmed repeatability and uniformity of the fuel compositions.

As Table 1 shows, the fuel contains Fe and SiO₂ as part constituents. Trace amounts of additional metal species, i.e., Al, Ni, Cr, Hg, and PbO were added as dopants during the fuel preparation.

2.3. Experimental procedure

The combustion experiments have been conducted with equivalence ratio varied around 0.2–0.3 to imitate the lean conditions used normally in the practical combustors (Niessen, 1995). Bottom ash was collected from the incinerator grate and the fly ash was collected in the fabric filter. In addition, the flue gas was sampled and...
analyzed for volatile metals (Pb and Hg) using a sampling port located at the exit from the bag-house.

Metals contents in the condensed combustion products (bottom ash and fly ash) were analyzed using atomic absorption spectroscopy (flame AA, Thermo Jarrel Ash, metal digestion using nitric acid solution). To insure the complete metal digestion, standard EPA method 3051 was used designed specifically for effective removal of metals from solid samples by heating them with nitric acid in a microwave oven. Metal compounds present in the ash have been determined using an X-ray diffractometer (a Phillips X’pert model).

The flue gas samples were collected using a gas-sampling manifold connected to three different sampling ports. To limit the sample loss and condensation, the sample collection tubes were heated to 110–130 °C and maintained at a pressure of 4–7 kPa above the atmospheric pressure. The flue gas was bubbled through an impinger solution of 1.5% potassium permanganate in 10% (3.6 N) sulfuric acid (Korpiel and Vidic, 1997). This solution was later analyzed by atomic absorption spectroscopy to determine the concentrations of Hg, Pb, and other metals in the flue gas.

2.4. Thermodynamic equilibrium estimates

The expected equilibrium combustion products produced at different equivalence ratios have been predicted using a thermodynamic equilibrium code (Selph and Hall, 1992). In the computations, the synthetic fuel was treated as a combination of representative species listed in Table 2. In addition, trace amounts of metals doped to the synthetic fuel (Al, Ni, Cr, Pb, Hg) as well as up to 0.5% of Cl were added to the fuel in different computation runs. The effect of chloride on the predicted metal partitioning was found to be negligible at these low chloride contents that are typical of the US MSW. The higher chloride contents were observed to affect significantly the metal phases and their distribution among the combustion products, but were not of interest to this investigation aimed at the characterization of the products of MSW incineration. The results of equilibrium computations performed in a wide range of equivalence ratios and some comparisons of the computed results versus the measured gas species concentrations have been discussed elsewhere (Thipse et al., 2001). In this paper, the focus has been placed at the equilibrium prediction of the metal-containing species and comparisons of the computations with the new experimental measurements. Therefore, the equilibrium computations were conducted only for the experimental fuel–air equivalence ratios (φ) ranging from 0.21 to 0.28.

Two sets of computations have been performed for each equivalence ratio. In the first computation, the adiabatic flame temperature was determined and the product species at these conditions were found. It has

Table 2
Synthetic fuel components, representative species and their enthalpies of formation used in the thermodynamic equilibrium computations

<table>
<thead>
<tr>
<th>Fuel component</th>
<th>Species</th>
<th>Formula</th>
<th>Enthalpy of formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newsprint (paper) hardwood mulch</td>
<td>Cellulose</td>
<td>C₆H₁₀O₅</td>
<td>906.3 (Brunner, 1989, Table 3)</td>
</tr>
<tr>
<td>Moisture</td>
<td>Water</td>
<td>H₂O</td>
<td>285.8 (Eremenko et al., 1998, Table 3)</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>Polyethylene</td>
<td>C₃H₈</td>
<td>51.2 (Cox and Pilcher, 1970, Table 3)</td>
</tr>
<tr>
<td>Iron</td>
<td>Iron</td>
<td>Fe</td>
<td>0</td>
</tr>
<tr>
<td>Animal feed</td>
<td>Methanamine</td>
<td>CH₃N</td>
<td>47.3 (Cox and Pilcher, 1970, Table 3)</td>
</tr>
<tr>
<td>Sand</td>
<td>Silica</td>
<td>SiO₂</td>
<td>910.9 (Eremenko et al., 1998, Table 3)</td>
</tr>
</tbody>
</table>
been assumed that the predicted species that are condensed at the adiabatic flame temperature can be considered as those forming the bottom ash. The gaseous products of the first computation have been considered as a fuel for the second computation (with the initial temperature equal to the adiabatic flame temperature), for which the final temperature has been pre-set to 300 K. The goal of the second computation was to compare the composition and phases of the cooled product species with those determined experimentally by analyzing the fly ash and flue gases exiting the incinerator.

The results of the equilibrium code computation are produced as mole fractions of various species, $C_{i}^{\text{eq}}$, where $i$ is the species counter. For a particular metal containing species, the equilibrium computation produced mole fraction $C_{m}^{\text{eq}}$. In order to compare this result with the atomic absorption measurement that produces the weight fraction, of a metal (as element) in the sample being analyzed, $m_{m}^{\text{AA}}$, the following re-normalization of the computational results was conducted. The computed (by the equilibrium code) mass percentage of each elemental metal $m_{m}^{\text{eq}}$, was calculated as

$$n_{m}^{\text{eq}} = \frac{\mu_{m} \times C_{m}^{\text{eq}}}{\sum_{i=1}^{N} \mu_{i} \times C_{i}^{\text{eq}}} \frac{\rho_{m}}{\rho_{m}^{\text{eq}}} \times 100\%,$$

where $\mu$ is the molar weight, $\rho$ is the density, subscript $m$ shows the predicted by the equilibrium code metal species (in most cases, metal oxides), and subscript m shows the elemental metal. Therefore, the calculated metal weight fraction, $m_{m}^{\text{eq}}$, could be compared directly with the metal weight fraction measured using atomic absorption techniques, $m_{m}^{\text{AA}}$.

### 2.5. Metal consumption rate estimates

The metal species fed into the primary combustion chamber are consumed through two main processes: heterogeneous oxidation and volatilization. The rates of these two processes need to be compared to the rate at which the metals are fed into the incinerator in order to evaluate the expected contents of various metal species in the combustion products. At the temperatures characteristic of the primary combustion chamber (around 1000 K), the group of metals including Fe, Ni, Cr, and Al are primarily oxidized heterogeneously, whereas Hg and Pb are volatilized. Therefore, to make an order of magnitude estimate for the volatile metals, their feed rates are compared to the expected rate of their volatilization based on a simplified energy balance approach. For the non-volatile metals, the feed rates are compared to the expected rates of their heterogeneous oxidation estimated at the temperature in the primary combustion chamber.

#### 2.5.1. Non-volatile metals

The synthetic fuel was doped with trace amounts (0.1 mass%) of Al, Ni and Cr, so that at different experimental fuel feed rates, the mass feed rates for these metals, $m_{t}$, varied in the range of 0.113–0.205 g/s. The fuel contained 8 mass% of iron, so that the experimental feed rate for Fe varied in the range of 9.04–16.4 g/s.

At the experimental temperature range of the primary combustion chamber, 1073–1273 K, the oxidation process for each of the non-volatile metals present in the fuel is best described by the parabolic law (Kubachewski and Hopkins, 1962)

$$\left(\frac{m_{\text{ox}}}{A}\right)^{2} = K_{p} \Delta t,$$

where $m_{\text{ox}}$ is the mass of the metal that has been oxidized during the time interval $\Delta t$, $A$ is the metal surface area, and $K_{p}$ is the parabolic rate coefficient. For a simple estimate, we assumed $\Delta t = 1$ s, so that the estimated $m_{\text{ox}}$ per second could be directly compared to the metal feed rate, $m_{t}$, also normalized per second. The following expressions were used to estimate the rate coefficient $K_{p}$ at the primary chamber temperatures:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Rate coefficient, $K_{p}$ (g$^{2}$ cm$^{-4}$ s$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.37 exp(−33,000/RT)</td>
<td>Stanley et al. (1951)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.2 × 10$^{2}$ exp(−68,300/RT)</td>
<td>Kubachewski and Hopkins (1962)</td>
</tr>
<tr>
<td>Al</td>
<td>2 × 10$^{-5}$ exp(−33,000/RT)</td>
<td>Kubachewski and Hopkins (1962)</td>
</tr>
<tr>
<td>Cr</td>
<td>61.5 exp(−64,630/RT)</td>
<td>Gülbransen and Andrew (1958)</td>
</tr>
</tbody>
</table>

The surface area for each metal was estimated as

$$A = 4\pi r^{2}N = \frac{3m_{t}}{\rho r},$$

where $r$ is the average size of the metal particles, $\rho$ is the metal density, and $N$ is the number of particles fed to the incinerator per second estimated as

$$N = \frac{m_{t}}{4/3\pi r^{3}\rho}.$$

The average particle sizes for each metal used in the synthetic fuel were determined using particle size distributions obtained from the optical microscopy measurements. The final results of these estimates i.e., the oxidation rates of non-volatile metals are shown in Table 3. The results indicate that at the primary com-
bustion chamber temperature range, iron is oxidized at a rate comparable to its feed rate and a more accurate estimate is needed to predict what portion of iron found in the bottom ash will be oxidized. Nickel and chromium can be oxidized at a noticeably faster rate than they are fed to the incinerator, therefore, it is expected that these metals be primarily contained in the bottom ash as respective oxides. For aluminum, the oxidation rate is slower than the feed rate, thus aluminum metal phase is expected to remain in the bottom ash.

2.5.2. Volatile metals

For these metals, their volatilization rate was compared with the feed rate. To estimate the volatilization rate, the heat required to preheat the metal to the boiling point and the latent heat of evaporation were balanced with the convective heat flow to the metal-containing particles. Different mechanisms of volatilization were considered for Hg and Pb.

Metallc mercury was added to the synthetic fuel and a simple boiling model was used for mercury. The expected rate of mercury evaporation, \( \dot{m}_{\text{Hg}} \), was estimated using the heat balance equation for mercury particles:

\[
4\pi r_{\text{Hg}}^2 N_{\text{Hg}} h (T_{\text{pcc}} - T_{\text{boil,Hg}}) = \frac{\dot{m}_{\text{Hg}}}{M_{\text{Hg}}} \left[ C_{P,\text{Hg}} (T_{\text{boil,Hg}} - T_0) + L_{\text{Hg}} \right],
\]

where \( r \) is the particle size, \( N \) is the number of “particles” fed to the primary combustion chamber per second, estimated using Eq. (4) above, \( M \) is the species molar mass, \( T_{\text{pcc}} \), is the temperature in the primary combustion chamber, varied from 1073 to 1273 K, \( T_{\text{boil,Hg}} \) is the mercury boiling point, \( T_0 \) is the initial fuel temperature, \( C_p \) is the molar heat capacity, \( L \) is the molar latent heat of vaporization, and \( h \) is the heat transfer coefficient, determined as \( k \cdot Nu/(2r)_{\text{Hg}} \), where \( k \) is the air thermal conductivity, and Nusselt number \( Nu \) is estimated using Whitaker equation (Cengel, 1997)

\[
Nu = 2 + \left[ (0.4Re^{1/2} + 0.06Re^{1/3})Pr^{1/3} \right]^{1/4} \left( \frac{\mu_s}{\mu_\infty} \right)^{1/4},
\]

where \( Re \) is the Reynolds number estimated using particle size and gas flow velocity in the combustion chamber, \( Pr = 0.69 \) is Prandtl number for air (Mills, 1995), and \( \mu_\infty \) and \( \mu_s \) are the air viscosities at the primary combustion chamber temperature and particle surface temperature, respectively.

The addition of lead to the synthetic fuel was in the form of condensed PbO\(_2\), and according to the literature data, PbO in presence of oxygen is further oxidized and volatilized as PbO\(_2\) at a temperature of \( T_\text{vol,PbO}_2 = 673 \text{ K} \) (Kubachewski and Hopkins, 1962). Therefore, lead volatilization was considered as a two-step process. In the first step, the condensed PbO\(_2\) formed as a result of PbO reaction with oxygen, and in the second step, the PbO\(_2\) was volatilized:

\[
PbO(s) + 1/2 O_2 \rightarrow PbO_2(s) \quad (7)
\]
\[
PbO_2(g) \rightarrow PbO_2(g) \quad (8)
\]

Both reactions are assumed to occur at 673 K, so that the heat balance equation used was

\[
4\pi r_{\text{PbO}}^2 N_{\text{PbO}} h (T_{\text{pcc}} - T_{\text{vol,PbO}_2}) = \frac{\dot{m}_{\text{PbO}}}{M_{\text{PbO}}} \left[ C_{P,\text{PbO}} (T_{\text{vol,PbO}_2} - T_0) + \Delta H + L_{\text{PbO}_2} \right],
\]

where the notation is similar to that used in Eq. (5) above and \( \Delta H \) is the enthalpy of reaction (7), estimated using enthalpies of formation of all reagents to be \(-75.9\) kJ/mol. The parameters used in the estimates are listed in Table 4 and the results of these estimates are summarized in Table 5. It is observed that both Hg and Pb can be volatilized noticeably faster than they are fed in the incinerator, so that it is expected that almost none of these metals should be found in the bottom ash.

### Table 3

<table>
<thead>
<tr>
<th>Metal</th>
<th>Feed rate (g s(^{-1}))</th>
<th>Oxidation rate (g s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T = 1073 \text{ (K)} )</td>
<td>( T = 1273 \text{ (K)} )</td>
</tr>
<tr>
<td>Fe</td>
<td>9.04</td>
<td>16.40</td>
</tr>
<tr>
<td>Ni</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>Al</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>Cr</td>
<td>0.11</td>
<td>0.20</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Overall ash compositions

Iron and silicon contents in the ash were determined using atomic absorption measurements; carbon, chlorine, hydrogen, nitrogen, and sulfur contents were obtained using standard ASTM chemical tests (ASTM, 1996). The remaining mass balance was assumed to be oxygen. The resulting compositions for both bottom ash and fly ash are illustrated in Fig. 2(a). In addition to the main elements, the ash percentage composed of the trace metals is lumped together and shown as the overall trace...
metal content labeled M. Compositions of the bottom and fly ashes predicted by the equilibrium computations are shown in Fig. 2(b). The relative metal contents in the ash predicted by equilibrium computations are much higher than the observed experimental metal concentrations. The main reason for this discrepancy is that the equilibrium computations do not predict the formation of carbon (soot) in the ash, whereas significant amounts of soot (and carbon) are found in both bottom and fly ash samples (cf. Figs. 2(a) and (b)).

Once this discrepancy is recognized, a superficial correction of the experimental bottom ash and fly ash contents can be suggested in which the elements that never appear in the predicted equilibrium ash composition, e.g., C, N, S and Cl, are removed from the experimental ash composition. Such “corrected” ash compositions can be compared versus the equilibrium computation results in order to approximately balance the overall quantities of metal-containing compounds and, most importantly, compare the magnitudes of their relative changes as a function of equivalence ratio. The recomputed experimental elemental compositions for the bottom ash and fly ash are shown in Fig. 2(c).

After each experimental run, the total masses of bottom ash $M_b$ and fly ash $M_f$ were measured. The total mass of the produced flue gas $M_g$ was calculated as $M_g = vA\rho t$, where $v$ is the flue gas velocity measured at the system exhaust using a pitot tube, $A$ is the area of the pipe cross-section where the velocity measurement was made, $\rho$ is the density of flue gas at a temperature of 373 K, and $t$ is the duration of the run. The gas density was estimated assuming that the gas composition was close to that predicted for the gaseous combustion products by an equilibrium computation conducted at the final temperature set to 373 K. Using the total masses of each of the combustion product component (fly ash, bottom ash and flue gas), and the measured concentrations of metal species in each of the components, the overall distributions of each metal between different combustion products were found. The results of this analysis are shown in Fig. 3 along with the results predicted by the thermodynamic equilibrium computations and some data reported in the literature. It can be noted that for all the metals except for Ni, our experimental data indicate higher metal species contents in the flue gas as compared to the other data sets reported in the litera-
An interpretation of this could be that in most of the referred works, electrostatic precipitators have been used, that are more efficient in capturing the ultrafine particles than the fabric filters used in this research. Therefore, it is likely that some of the fine and ultrafine particles escaped the fabric filter and remained aerosolized in the flue gas. Some of that fine particulate matter could be captured during the gas sampling and,

Fig. 2. Compositions of the bottom and fly ashes: (a) experimentally produced samples, (b) compositions predicted by the equilibrium computations, (c) modified experimental compositions.

therefore, increased concentrations of metal species in the flue gas could be detected by the atomic absorption spectroscopy measurements.

The overall amounts of the metals entering the system as a part of the fuel have been balanced with the respective metal contents in the combustion products determined using the total mass and atomic absorption measurements for the flue gas and fly and bottom ash. The results of comparison of the overall amounts of metals in the input and output of the incinerator are illustrated in Fig. 4. Estimates show that the experimental errors in the analyses of the ash metals contents can account for approximately 10% of the difference between the metal mass input and output. As shown in Fig. 4, the observed discrepancy in noticeably greater only for mercury. It is suggested that for the most part, this discrepancy is due to the ultra-fine mercury containing particles that escaped the bag-house filter and have not been effectively captured during the flue gas sampling.

The phases present in the bottom ash and fly ash have been identified based on the X-ray diffraction measurements. Typical X-ray diffraction patterns for the bottom ash and fly ash samples are presented in Fig. 5. Analyses of such patterns produced by the ash samples have not been straightforward due to a large number of peaks resulting from the complex phase composition. Therefore, only the strongest peaks have been accounted for and respective phases are marked in Fig. 5. A more detailed discussion of the observed metal phases follows below.

3.2. Metal phases and partitioning in the combustion products

3.2.1. Iron

Iron is a non-toxic, environmentally benign element and often the researchers motivated to determine the environmental and health hazards of the combustion products do not consider its partitioning and phases found in the ash. However, iron is one of the most significant constituents of the produced ash and a number of chemical reactions involving iron and other metals can occur. In addition, the processes of oxidation and condensation of the iron-containing species and produced iron-containing airborne particles can affect both chemical and physical aerosol processes occurring in the incinerator. Therefore, understanding of the formation
Mechanisms and distribution of the iron species is important for understanding the behavior of toxic trace metal elements.

The equilibrium computations predicted formation of Fe₂O₃ as the only iron-containing species in the bottom ash and FeOOH as the only iron-containing species in the fly ash. In each case, the computations predicted the presence of only one iron-containing condensed species, even though the thermodynamic data for a number of compounds, including FeO, Fe₃O₄, FeCl₂, FeCl₃, FeS, FeS₂, and FeO₄S, and have been available in the thermodynamic database (the data for iron silicates have not been available). Some of the equilibrium computations reported in the literature suggest the formation of additional iron-containing species, such as FeCl₃ and FeSO₄, e.g., Verhulst et al. (1996). The main difference between the equilibrium computations conducted in this project and those by Verhulst et al. (1996) is in the initial chloride content. The chloride fuel content used in our computations (and experiments) was 0.5%, the reported chloride content of MSW in the United States, whereas up to 3% of chloride have been added to the fuel by Verhulst et al. (1996).

In terms of the iron partitioning between the fly ash and bottom ash, our equilibrium computations are in fair agreement with the earlier measurements by Brunner and Monch (1986), and Wang and Chiang (1999), as illustrated in Fig. 3. However, as shown in Fig. 3, our AA measurements indicate significantly higher iron contents in both fly ash and flue gas as compared to the predicted or measured earlier contents. (Note that here and below the results of the atomic absorption measurements are corrected as shown in Fig. 2(c).) One possible reason for such a discrepancy has been discussed by Wu et al. (1994), based on the possibility of the mechanical entrainment of non-volatile metal particles into the turbulent gas flows. This effect could be more significant in our experiments than in industrial incinicators because relatively small iron particles (800 μm average diameter) were added to the synthetic fuel as opposed to large bulk iron pieces often contained in the municipal waste. The estimated settling velocity for the iron particles is about 10 m/s, that is less than the gas velocity in the combustion chamber of about 15 m/s, so that the entrainment of the particles could indeed occur.

The computations showed that the content of Fe₂O₃ (and thus, the overall iron content in the bottom ash) increases at higher equivalence ratios, whereas the FeOOH content, or the total iron content in the fly ash, decreases at higher equivalence ratios. This trend is in agreement with the AA measurements, as shown in Fig. 6.

Phases of iron in both the bottom ash and fly ash were determined using X-ray diffraction (XRD). The XRD measurements indicated the presence of common species, Fe, Fe₂O₃ and FeO in both bottom and fly ash samples. Also, such species as Fe₁₄SiO₄ were detected in the bottom ash and FeOOH with Fe₃Si were detected in the fly ash (Fig. 5). Perhaps, the most unexpected observation is the presence of metallic iron in the fly ash. Two mechanisms that could explain such observation can be considered. One mechanism has been discussed by Senior et al. (2000), who suggested that iron oxide formed in the primary combustion chamber could be vaporized through its reduction. Later on, the ultra fine iron particles could condense on the fly ash particles in the heat exchanger/filter area that is lean in oxygen (the gas is a mixture of nitrogen and carbon dioxide). The other mechanism could simply be the mechanical entrainment of iron particles in the flue gas.

The changes in the intensities of the X-ray diffraction peaks qualitatively reflect the changes in the relative concentrations of the Fe-containing species. Quantities of Fe and Fe₂O₃ in the bottom ash increased at higher equivalence ratios, whereas the content of FeO decreased. In contrast, quantities of Fe, Fe₂O₃ and FeOOH in the fly ash decreased at higher equivalence ratios, whereas the content of FeO increased. This
behavior can be understood considering that in a typical fuel-lean system (e.g., in the primary combustion chamber), the chemical reaction rate of the iron oxidation is accelerated at higher equivalence ratios. The primary product of iron oxidation is an Fe$_2$O$_3$ layer on the Fe particle surface. Thus, the faster formation of such a layer results in a slower iron reaction producing intermediate products, e.g., volatile FeO, FeOOH, and, possibly, gaseous Fe, ultimately causing the decrease in the contents of these species in the fly ash. Thus, the observed decrease in the elemental Fe content in the fly ash at higher equivalence ratios indicates that the primary mechanism for its transfer into the fly ash is through the chemical reduction/vaporization/re-condensation route, as opposed to the simple mechanical entrainment of iron particles.

Clearly, there are more of the iron-containing phases observed to be present in the ash as compared to the equilibrium predictions. A more detailed kinetic modeling and a more detailed investigation of the structure and compositions of the ash particles would be needed for an adequate interpretation of these observations important for the understanding of the overall structure and composition of the produced ash.

### 3.2.2. Silicon

The equilibrium computations predicted that SiO$_2$ is the only silicon-containing species in both the bottom ash and the fly ash. At the same time, the XRD measurements indicated the presence of additional silicon containing species, including SiC, Fe$_4$SiO$_4$ and Si in the bottom ash and Fe$_3$Si in the fly ash. It has been reported that the elemental Si could form in the incinerator chamber when local oxygen depleted reduction zones are developed (Wey et al., 1998). In this case, the silicon oxide SiO$_2$ contained on the fuel grate can be reduced to the volatile SiO and pure Si through the following reactions:

$$\text{SiO}_2 + \text{CO} \rightarrow \text{SiO} + \text{CO}_2 \quad (10)$$

$$\text{SiO} + \text{CO} \rightarrow \text{Si} + \text{CO}_2 \quad (11)$$

As shown in Fig. 7, it is predicted by the equilibrium computations that at higher equivalence ratios the content of silicon in the fly ash increases and in the bottom ash decreases. This predicted trend is due to higher temperatures, and thus, higher overall SiO$_2$ vapor pressure at higher equivalence ratios. Although the experimental temperatures at higher equivalence ratios are indeed higher, the experimentally determined changes in the silicon content in the fly and bottom ashes are opposite to those predicted to occur in equilibrium (Fig. 7). This discrepancy is most likely due to a slow kinetics of the reaction of SiO$_2$ contained in the fuel, which results in a faster accumulation of the SiO$_2$ in the bottom ash at a faster fuel feed rate, e.g., at higher equivalence ratios.

The relative changes in the intensities of the X-ray diffraction peaks show qualitatively that the contents of Si and SiO$_2$ in the bottom ash increase at higher equivalence ratios while the SiC content decreases. This observation can be interpreted as a result of a more complete carbon oxidation occurring at higher equivalence ratios, so that less of carbon remains available to react with silicon to form SiC. At the same time, the higher rate of chemical reaction between oxygen and SiO$_2$ results in a faster reduction of SiO$_2$ to Si, as described above.

Concentrations of both Fe$_3$Si and SiO$_2$ in the fly ash decrease at higher equivalence ratios, the trends that are likely caused by a faster rate of iron oxidation and a faster rate of oxygen reaction with hydrocarbon species in the primary combustion chamber.

### 3.2.3. Aluminum

Our equilibrium computations predicted formation of Al$_2$O$_3$ in both bottom ash and fly ash. The formation of AlCl$_3$ has been predicted by (Verhulst et al., 1996) using significantly higher chlorine contents in the fuel. At the same time, the estimates of the rates of hetero-
geneous reaction showed that substantial amounts of unreacted aluminum should accumulate in the bottom ash. The Al contents in the bottom ash and fly ash measured by AA remain almost unchanged at varied equivalence ratios, as shown in Fig. 8. Thus, the change in the distribution of aluminum species between the bottom ash and fly ash is smaller than the equilibrium prediction, indicative of the defining role of the slow oxidation kinetics on the aluminum behavior in the primary combustion chamber.

Distributions of the aluminum-containing species between the fly ash, bottom ash, and flue gas reported in the literature (Verhulst et al., 1996; Wang and Chiang, 1999) and in this paper are shown in Fig. 3. The quantity of Al in the fly ash produced in these experiments (about 5%) is consistent with those reported in the literature (4–5%). A somewhat higher aluminum content in the flue gas measured in these experiments could be explained by the presence of the ultra fine alumina particles entrained in the gas that escaped the fabric filter.

3.2.4. Chromium and nickel

The equilibrium computations predicted that oxides Cr$_2$O$_3$ and NiO are produced in both the bottom and fly ashes (Figs. 9 and 10). The reaction rate estimates showed that the heterogeneous reaction of oxidation is fast compared to the feed rate, and thus most of the oxides should form in the bottom ash. The rate of volatilization of these oxides at the primary combustion chamber temperature of around 1000 K is expected to be slow because of their very high boiling temperatures. The AA measurements indeed show that the amounts of chromium and nickel in the bottom ash are greater than predicted by the equilibrium computations (Figs. 9 and 10). The directions of the changes in the distribution of chromium and nickel between the fly and bottom ash predicted to occur by the equilibrium computation are in agreement with the experimental trends, however the magnitude of the predicted changes significantly exceeds that observed experimentally. This discrepancy, similarly to the earlier discussion for aluminum, could be indicative of a slow chemical kinetics controlling the behavior of chromium and nickel oxides.

The experimental distributions of the Cr and Ni-containing species between the bottom ash, fly ash and flue gases determined in this project are in good agreement with the results reported by Binner et al. (1997), who also used fabric filters to collect the fly ash (cf. Fig. 3). A noticeably higher percentage of the Cr-containing species has been found in the fly ash by Wey et al. (1998), who used electrostatic precipitator filters for capturing the fly ash. Therefore, it is possible that a
significant portion of the chromium containing species comprises of the very fine particles that escape the fabric filters used in this research and in the experiments by Binner et al. (1997).

3.2.5. Mercury and lead

The equilibrium computations predicted formation of the condensed HgO and PbO oxides in the bottom and fly ashes and gaseous HgO and PbO in the flue gas. Both the mercury and lead oxide contents decrease in the bottom ash and increase in the fly ash and the flue gas at increased equivalence ratios (cf. Figs. 11 and 12). These trends are in qualitative agreement with the results of the atomic absorption measurements shown in Figs. 11 and 12. However, the absolute amounts of mercury and lead found in the flue gas exceed by about an order of magnitude the amounts predicted to be gasified in equilibrium. In the overall distribution between the fly ash, bottom ash and the flue gas, a much lower percentages of both mercury and lead are found in the fly ash in these experiments as compared to the data reported in the literature (see Fig. 3). The rates of volatilization of both metals are estimated to be higher than their feed rates into the primary combustion chamber. Thus as discussed above, gaseous Hg and PbO2 are produced in the primary combustion chamber. The following reactions are accompanied by the condensation of mercury and lead oxides from the gas phase and, therefore, it is expected that significant amounts of the condensed oxides will comprise of ultra-fine particles. Therefore, using of fabric filters in this research could again account for the discrepancy in partitioning of mercury and lead between the fly ash and flue gas observed in this work and reported by other researchers using electrostatic precipitation filters (Brunner and Monch, 1986; Nakamura et al., 1996) or wet scrubbers (Vogg et al., 1986).

4. Conclusions

An experimental technique was developed for studying metal partitioning in the products of waste incineration. The technique exploits a continuous feed, pilot-scale incinerator facility and well-characterized and reproducible synthetic fuel imitating the MSW. The total amounts of metals in different components of combustion products were determined using atomic absorption spectroscopy. The phases of different metals in fly and bottom ash were determined using X-ray diffraction and compared with the product compositions expected based on the thermodynamic equilibrium estimates. It was observed that the effect of chlorine on metal partitioning becomes important when chlorine contents in the fuel significantly exceed 0.5%, the typical chlorine contents in the US MSW. The results on the overall metal partitioning between the fly ash, bottom ash, and flue gas are in reasonable agreement with the earlier experimental reports. One of the significant discrepancies observed was that smaller than usual metal contents were found in the fly ash. It is suggested that the use of the fabric filters inefficient in capturing the fine particulate matter caused that discrepancy. Mechanical entrainment of metal particles in the turbulent gas flow in the primary combustion chamber was indicated to be important in transferring iron oxides into the fly ash. It has been also found that the sequence of iron oxidation, reduction, vaporization, and condensation has occurred and caused production of elemental iron in the fly ash. Because of the large absolute iron concentration in the municipal waste and its combustion products, this sequence is important for the understanding of the overall ash particle formation mechanisms. Evidence of another
reduction process, formation of elemental Si from SiO₂, has also been found. Such processes need to be considered in modeling the waste incineration because of their effect on the flame exothermicity and mechanisms of the formation of bottom ash. It has also been observed that the slow kinetics of such processes as oxidation of Al and volatilization of oxides of Cr and Ni needs to be considered to adequately describe the behavior of these metals in the furnace and caution should be exercised when the thermodynamic equilibrium predictions are used. Finally, the results indicate that significant amounts of the lead and mercury-containing species comprise of very fine particles that are not effectively captured by the fabric filters.

It is suggested that a more detailed characterization of the phases and morphology of the fly and bottom ashes be conducted to better understand the processes and conditions affecting the ash formation and metal species partitioning. It is also suggested that for a future research, a new electrostatic precipitation filter system should be installed in the NJIT pilot scale combustor facility to enable capturing the fine fly ash particles.

References


