

Modeling Kinetics of Cd, Pb, and Zn Vaporization during Municipal Solid Waste Bed Incineration

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The fate of heavy metals contained in municipal solid waste is of major concern in the incineration process. This study is the first attempt to analyze the kinetic behavior of Cd, Pb, and Zn in a waste bed burning on the grate of an incinerator. The vaporization rates of the three heavy metals were derived from laboratory experiments. The kinetic law was then introduced into Garbed-ss, a mathematical model of the on-grate incineration of a refuse bed. Results show that the calculated vaporization of the three metals is fast, proceeds to nearly full completion, occurs at the pyrolysis front, and is indeed controlled by the thermal degradation of the waste. Although in agreement with thermodynamic calculations, the vaporization of lead and zinc seems to be overestimated. The model would be improved by accounting for the initial physical and chemical speciation of the heavy metals in the waste feed.

Introduction

Incineration of municipal solid waste (MSW) offers the advantages of achieving waste-to-energy conversion, dramatically reducing the waste volume and turning it into inert matter, bottom ash. However, this high-temperature process may also promote the formation of a number of pollutants, such as heavy metals (HM), NO_x, VOC, and dioxins. Excellent control of the process and an efficient exhaust gas cleaning system are therefore required for its safe operation. The fate of HM originally contained in MSW is a major concern. Depending on waste composition and operating conditions, HM can leave the process in the bottom ash, in the boiler and filter ashes collected from the fumes, or, at worst, in the stack gas.^{1,2} It would be highly desirable to be able to predict the evolution of HM in the incineration process, particularly their partition between gas and solid from the burning waste bed. The present Article is the first attempt to calculate the rates and amounts of Cd, Pb, and Zn released from the burning waste bed at typical incineration conditions, using a new approach that combines experimental vaporization kinetics and the use of a mathematical model of a MSW bed in combustion.

Literature reports several studies that consider the HM evolution from a thermodynamic point of view.^{3–5} From the composition of the waste and of the gas, the speciation of HM, that is, their distribution into chemical species, was predicted. Although useful and often in qualitative agreement with ash analyses, the thermodynamic calculations cannot predict the rates of HM vaporization. In some studies, these were determined experimentally, using either model fuels^{6,7} or real waste impregnated with metallic salts.^{8,9} Integrating such kinetic results into a mathematical model of bed incineration would enable one to calculate the actual fate of HM as a function of local operating conditions, as shown hereafter.

Fluidized Bed Experiments of Vaporization of Heavy Metals

In their recent papers, Falcoz et al. studied the kinetics of HM vaporization from “real artificial” waste pellets made from

MSW in a laboratory fluidized bed reactor.^{8,9} These synthetic pellets were made from real MSW, sand, and wallpaper glue. Samples were doped with HM by impregnating flakes of MSW in a liquid solution of metal salt; the mixture was shredded, pressed into cylindrical pellets, and dried. The procedure used for experiments is as follows. Once the reactor is at steady state (desired temperature reached and operating conditions maintained), a given amount of model waste is injected into the fluidized bed. The evolution of the metal concentration in exhaust gases is measured online by a specific ICP-OES (inductively coupled plasma-optical emission spectrometry) technique, with experimental details as already reported.⁸ Experiments were carried out with Cd, Pb, and Zn at 650, 680, 710, 740, 770, and 800 °C. Raw results are treated by an inverse method, from which the curves of the rate of vaporization of a HM as a function of the metal content remaining in the waste are derived. These curves obviously depend on temperature, but are virtually independent of the other experimental conditions. This is obtained through the procedure itself: the fluidized bed gives high transfer rates, and the inverse method accounts for the flow and mass transfers. Figure 1 shows the results for the three metals at 680 and 800 °C.

From the initial concentration q_0 (on the right-hand side), the rate r first quickly increases to a maximum r_{\max} , from which it progressively decreases to zero at a final value q_f . The first

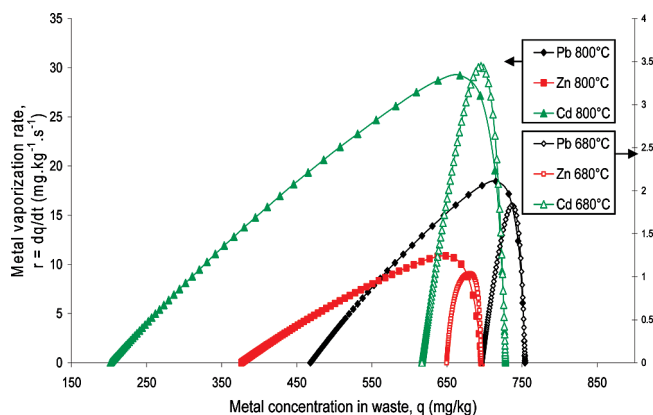


Figure 1. Vaporization rate of Cd, Pb, and Zn at 680 and 800 °C, obtained from Falcoz et al.⁹

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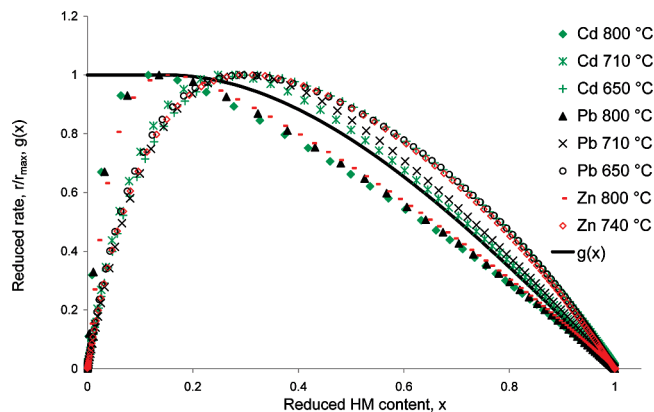


Figure 2. Overall kinetic law used, expressing the vaporization rates of Cd, Pb, and Zn, obtained from Falcoz et al.⁹

increase is a short transient period of little physical meaning, whereas the decreasing rate period corresponds to an increasingly difficult vaporization as the metal content decreases.

These experimental kinetic laws must be given an analytical expression to enable them to be used in the bed combustion model. Two approaches were proposed by Falcoz et al. In the first one,⁸ a specific expression is obtained by polynomial fitting for each metal studied, possibly distinguishing between low (<740 °C) and high (≥ 740 °C) temperatures. In the second one,⁹ after a change of variables, a single overall (valid for the three metals) kinetic law has been derived. This law is represented in Figure 2, and its mathematical expression is the following:

$$\text{If } x \leq x_m \text{ then } g(x) = 1$$

$$\text{If } x > x_m \text{ then } g(x) = \frac{1}{2} \left(\frac{x - x_m}{1 - x_m} \right)^3 - \frac{3}{2} \left(\frac{x - x_m}{1 - x_m} \right)^2 + 1$$

$$\text{where } x = \frac{q_0 - q}{q_0 - q_f}, x_m = 0.15, g(x) = \frac{r}{r_{\max}}, \text{ and } r_{\max} = k_0 e^{-(E_a/RT)} \quad (1)$$

The first part (from $x = 0$ to 0.15) of the curves only accounts for less than 5% of the vaporized amounts and was replaced for sake of simplification and physical consistency with a constant rate period.⁹ Physically, obtaining a unique relationship mostly reflects the influence of the solid matrix on the release of a HM from the solid. The specific properties of the HM itself are embedded in r_{\max} and q_f . Numerical values of k_0 , E_a , and q_f for Cd, Pb, and Zn are given by Falcoz et al.⁹

Mathematical Model of a Burning MSW Bed

Asthana et al. developed a 2-D steady-state model for simulating on-grate municipal solid waste incineration.¹⁰ This model, named GARBED-ss, describes the main physical, chemical, and thermal phenomena involved in the combustion of an MSW bed on a traveling grate of an incinerator: gas–solid reactions, gas flow through the porous waste particle bed, conductive, convective and radiative heat transfer, drying and pyrolysis of the feed, the emission of volatile species, combustion of the pyrolysis gases, the formation and oxidation of char and its gasification by water vapor and carbon dioxide, and the consequent reduction of the bed volume. The kinetics of pyrolysis of cellulosic and noncellulosic materials were experimentally derived from experimental measurements. Calculated variables include solid and gas temperatures, compositions, velocities, and reactions rates. The model was validated against pilot-pot experiments. Details on this have been reported in our previous works.^{10,11}

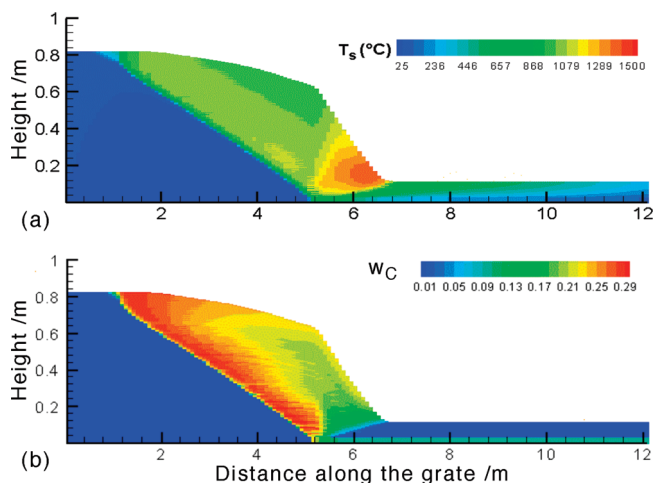


Figure 3. Typical results of GARBED-ss model: maps of solid temperature (a) and weight fraction of char (b).

Examples of calculated results, which will be helpful when subsequently discussing the HM behavior, include maps of the solid temperature and of the weight fraction of char throughout the bed at typical incineration conditions (Figure 3). The simulated operating conditions, as well as the geometrical characteristics of the facility, correspond to the MSW incinerator of Strasbourg, France. The waste feed was 11 tons h^{-1} , and the primary air flow rate was 30 000 $\text{m}^3_{\text{STP}} \text{h}^{-1}$, injected at 25 °C. The set of three grids was 12.15 m long. More details are given in the Supporting Information of our previous work.¹⁰

The highest temperatures were found above the pyrolysis front (approximately 1100 °C, $z = 2\text{--}5$ m), in the narrow zone where the pyrolysis gases burn and where char, the carbonaceous residue of the pyrolysis, is formed, and above the front of combustion of char (the hottest zone, approximately 1250 °C, $z = 5\text{--}7$ m).

Heavy Metal Vaporization

Speciation. Heavy metals are encountered in MSW in a variety of chemical compounds (metals, oxides, mixed metal oxides, sulfates, sulfides, etc.), mostly depending on the type of waste.^{12–14} At the high temperatures achieved in incinerators, most of these metal-bearing compounds can vaporize, forming chemical compounds as dictated by thermodynamics: simple metal vapor, metal chloride, metal sulfide, metal oxide, etc. Local thermodynamic calculations based on the calculated values of temperature and gas composition help to visualize the full speciation of HM in a burning MSW bed. Figure 4 shows the results of Menard et al.⁵ in the case of lead, which, from thermodynamics, should vaporize in the entire hot zone of the bed, forming Pb(g) , PbS(g) , PbCl(g) , $\text{PbCl}_2(\text{g})$, and PbO(g) . Cadmium and zinc should also vaporize, the gas species expected being only Cd(g) and $\text{CdCl}_2(\text{g})$, and Zn(g) and $\text{ZnCl}_2(\text{g})$, respectively.

Physical and Chemical Processes. When heated, an HM contained in the MSW feed will either (i) vaporize under a chemical form dictated by thermodynamics that may differ from its original form, which for simplicity will hereafter be referred to only as HM, (ii) transform into another, more stable, solid species, (iii) remain unchanged, or (iv) be released as a result of the thermal degradation of the organic matrix in which it was trapped. Events (ii) and (iii), which do not involve vaporization, will not be dealt with here. The vaporization (i) of a HM, that is, the reaction

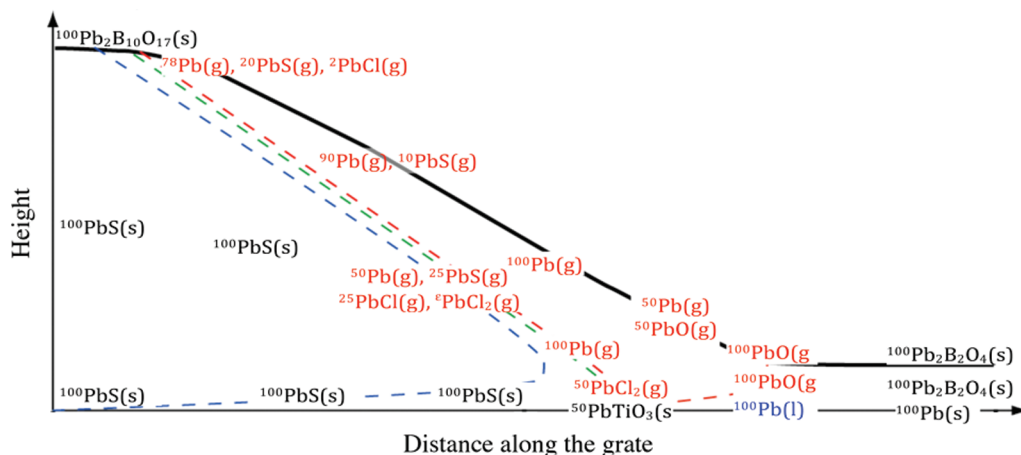
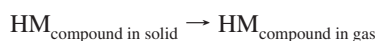


Figure 4. Speciation of lead in a burning MSW bed, obtained from Menard et al.:⁵ (s) solid phase, (c) condensed phase (solid or liquid), (g) gaseous phase. The left exponent figure indicates the molar percentage of the metal found in that species at equilibrium.



is a heterogeneous process and as such is accompanied by a mass transport process, the outward diffusion of the produced gas species from the waste particle. Both processes may control the overall rate of vaporization. Additionally, the thermal degradation of the waste, that is, its pyrolysis or combustion, interferes with vaporization (iv). Depending on the relative rates of those processes, different situations may occur, as shown in Figure 5.

According to the recent findings of Mazza et al.,¹⁵ the overall HM vaporization from waste particles in a fluidized bed takes place according to scheme (a) at low temperatures (below 750 °C), limited by gas diffusion through the metal-free outer layer of the unburnt waste particle, and according to scheme (d) at high temperatures (above 750 °C), with an HM release controlled by the thermal degradation of the waste, which occurs much more rapidly than vaporization. These authors developed a specific numerical particulate model for simulating these processes. However, such a particulate model involves meshing of the particles, which dramatically increases the computing time when modeling a 2D multiparticle system such as an MSW bed. Furthermore, in our case, the thermal degradation of the waste was already modeled in GARBED-ss; we thus preferred the simpler approach detailed below.

Model of Heavy Metal Vaporization from the Bed

Calculation of the Vaporization Rate. For modeling the HM release in the burning bed, the vaporization rate must be calculated as a function of local conditions, especially temperature. We considered that the overall kinetic law given above (eq 1), derived from experiments with artificial real waste pellets, accurately reflects the processes of HM vaporization and of subsequent gas transport out of the waste particles and can be directly used for calculating the overall vaporization rate. However, two adaptations had to be made.

First, the kinetic variables in GARBED-ss are the rates per unit volume of the bed and extents of reactions. In the case of vaporization of an HM, the extent is defined as

$$X_{\text{HM}} = 1 - \frac{m_{\text{HM}}}{m_{\text{HM}_0}} = 1 - \frac{w_{\text{HM}}}{w_{\text{HM}_0}} M_s \text{ with } M_s = \frac{m_p}{m_{p0}}$$

where m_{HM} is the mass of HM in a waste particle of mass m_p , w_{HM} its weight fraction, and M_s is the fraction of the initial (subscript 0) mass of the burning waste particle. M_s and its time

derivative r_{M_s} are routinely calculated by GARBED-ss. The rate of vaporization of a HM per unit volume of the bed $r_{\text{HM,bed}}$ (in $\text{kg}_{\text{HM}} \text{m}_{\text{bed}}^{-3} \text{s}^{-1}$) is then calculated from the experimental rate r (in $\text{mg}_{\text{HM}} \text{kg}^{-1} \text{s}^{-1}$) of eq 1 as follows:

$$r = r_{\text{max}} g(x) = k_0 e^{-(E_a/RT)} g(x)$$

$$r_{\text{HM,bed}} = \rho_{\text{app0}} (10^6 r_{M_s} - r_{M_s} w_{\text{HM}})$$

where ρ_{app0} is the initial apparent density of the MSW feed bed. In the last equation, the first term of the right-hand side represents the rate of HM release by vaporization (including possible limitation by internal diffusion), and the second term represents the rate of HM released as a result of the thermal degradation of the waste (pyrolysis or combustion).

Second, additional external mass transfer resistance may a priori occur in the packed bed of MSW on-grate through the boundary layer around the waste particles, which was negligible in the fluidized bed experiments. We included this possible resistance using the concept of the additive reaction times.^{11,16} In practice, the calculated results showed a posteriori that this resistance was negligible.¹¹

Transport in the Bed. Finally, the overall vaporization rate being known, the transport of the HM in the MSW bed of a grate incinerator can be modeled, both in the solid and in the gas phases, via

$$\begin{aligned} \frac{\partial}{\partial x} (\rho_{\text{app}} v_s w_{\text{HM}}) &= -r_{\text{HM,bed}} \\ \frac{\partial}{\partial x} (\rho_g v_x y_{\text{HM}}) + \frac{\partial}{\partial z} (\rho_g v_z y_{\text{HM}}) &= r_{\text{HM,bed}} \end{aligned}$$

where x and z are the distance along the grate and the height in the bed, respectively, v_s is the velocity of the solids, v_x and v_z are the two components of the gas velocity, ρ_g is the gas density, and y_{HM} is the weight fraction of HM in the gas phase.

Three sets (for Cd, Pb, and Zn) of the last five equations were added to the standard GARBED-ss code to provide it with the capability of predicting the behavior of heavy metals.

Results and Discussion

The evolution of Cd, Pb, and Zn during a typical MSW incineration operation was calculated following the previous approach. In addition to considering HM, the other input conditions were the same as for the simulation, the results of which are given in Figure 3; let us recall that the operation is

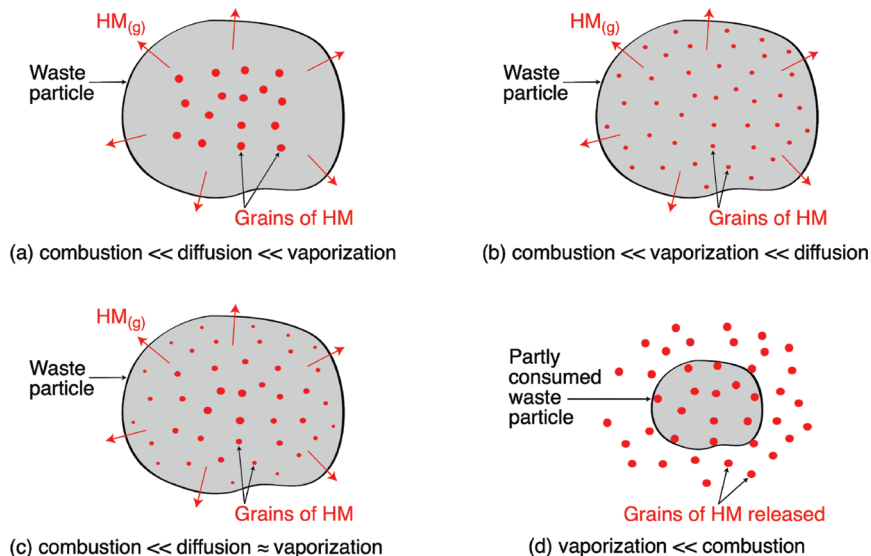


Figure 5. Vaporization of a HM from a burning waste particle (\ll means much slower than).

Table 1. Initial and Final Contents of HM in the Waste Bed

metal	initial weight fractions in MSW	fraction of initial content remaining in the bottom ash
Cd	15 ppm	2.6%
Pb	820 ppm	4.0%
Zn	1100 ppm	2.1%

steady-state. The initial contents in Cd, Pb, and Zn, given in Table 1, are assumed to be uniform in every waste particle. The values were taken as representative upper limits of the usual range of these HM in MSW.¹⁷ Figure 6 shows the calculated maps of the extent of vaporization for the three metals.

These results first express that the three metals are almost fully vaporized from the bed. Vaporization takes place in a limited hot zone, which coincides with the pyrolysis front (Figure 3b). The process is fast, as the advancement goes from

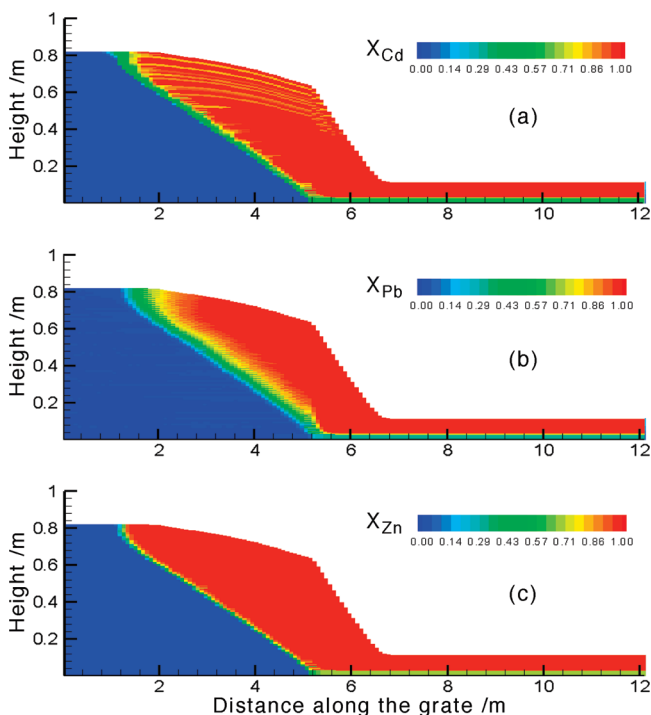


Figure 6. Fraction of Cd (a), Pb (b), and Zn (c) vaporized from the bed.

0 to about 1 in less than 0.5 m. This can be explained by the high temperatures encountered in this zone (Figure 3a). Indeed, because temperature increases abruptly, the kinetics of the vaporization themselves seem to be of little influence, and HM are mostly released as the result of the thermal degradation of the solid, that is, at a rate equal to the pyrolysis rate. This also explains why the behaviors of the three metals are very similar. Downstream and at the bed end, significant fractions of HM are just found confined to a thin layer on the grate. This layer was only heated for a short period and at temperatures that never exceeded 800 °C. According to the calculations, only a few percent of the initial contents in Cd, Pb, and Zn are left in the bottom ash (Table 1).

Those results agree well with the thermodynamic calculations of Menard et al.,⁵ which predict a large zone of stability of the gaseous forms of the considered HM, and thus a possible full vaporization of the three metals but suffer from the same shortcoming: the vaporized amounts of Zn and especially Pb seem overestimated. From analyses of the bottom ash after combustion, as much as 60% of Pb can remain. The following reasons may be advanced as explanations for this discrepancy, in order of increasing likelihood. (i) A possible recondensation of the HM vaporized in the lower layers could occur above, in colder layers, as with moisture in the iron ore sintering process.¹⁸ However, the calculated map of temperatures does not exhibit such cold regions above the vaporization front. (ii) The vaporization kinetics measured using the real artificial waste pellets are inaccurate (too fast). However, their effect is finally limited because the overall HM release is essentially controlled by the rate of pyrolysis of the bed. (iii) The present model, despite its success for simulating the incineration process, oversimplifies the HM evolution. In this respect, some arguments given by Menard et al.⁵ should be recalled here. Lead, for example, is not uniformly distributed in MSW. Only about one-third is found in combustible components, the major part being a component of glass and massive objects, inert in combustion, and its initial speciation involves oxides that are rather poorly volatile.¹⁹ That could explain a much lower vaporization than predicted. For zinc, many stable solid species exist at low and also intermediate temperatures, from which vaporization could be impeded. Therefore, we believe that it would be necessary to more precisely account for the initial physical and chemical forms of HM in MSW to more accurately predict their complete

evolution during incineration. A knowledge and description of their partition between combustible and incombustible components seems a first requisite.

Beyond, with the prospect of future work, the evolution of HM downstream the bed, that is, in the combustion chamber, the boiler, and the fume treatment system, should be considered. Metal species can further transform chemically, as studied by Menard et al.,⁵ and physically. In particular, condensation can occur on airborne particles, including particles carried over the bed as a result of bed mixing and high gas flow.

Conclusion

We investigated the behavior of three HM (Cd, Pb, and Zn) initially contained in MSW during the combustion of a waste bed traveling on the grate of an incinerator. The followed approach was based on a previously developed mathematical model of the combustion of the MSW bed, GARBED-ss, to which a kinetic description of the vaporization of HM from the waste particles was added. The vaporization kinetics were taken from Falcoz et al.,⁹ who derived them from specific HM vaporization experiments on real artificial waste pellets doped with HM and burned in a laboratory fluidized bed. Calculated results at typical incineration conditions show that the vaporization of the three HM is fast, proceeds to near completion, and occurs in a narrow zone coinciding with the pyrolysis front. The fast heating rates encountered by the solids and the high temperatures attained make the overall vaporization process controlled by the rate of pyrolysis. The small amounts of HM remaining in the bottom ash at the discharge end of the grate are concentrated in a thin layer close to the grate, which is not sufficiently heated to cause full vaporization.

The results are in accordance with thermodynamic predictions, but the vaporization of Pb and Zn seems overestimated. This work was the first attempt to model the kinetics of HM vaporization from a burning waste bed. An average description of the waste particles was adopted, with uniformly distributed HM contents. However, it appears from the results that this model still needs improvements. In particular, the initial physical and chemical forms of the HM and their distribution among the MSW feed should be taken into account.

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