Development of an inverse method to identify the kinetics of heavy metal release during waste incineration in fluidized bed

S. Abanades [a,*], G. Flamant [a], D. Gauthier [a], S. Tomas [a], L. Huang [b]

[a] *Processes, Materials, and Solar Energy Laboratory (PROMES-CNRS, UPR 8521), B.P.5 Odeillo, F-66125 Font-Romeu Cedex, France*
[b] *State Key Laboratory of Coal Combustion (SKLCC-HUST), Huazhong University of Science and Technology, 430074 Wuhan, PR China*

Abstract

This paper deals with the emission of heavy metals (HM) during the incineration of municipal solid waste in a fluidized bed reactor. This study focused on the development of a general method to identify the kinetics of vaporization of heavy metals from the on-line analysis of exhaust gas. This method is an inverse method, which requires only the time evolution of the HM concentration in exhaust gases (experimental data) and a global bubbling bed model developed for transient conditions at the reactor scale.

First, a lab-scale fluidized bed incinerator was set-up to simulate the HM release during the thermal treatment of metal-spiked model wastes. A specific on-line analysis system based on ICP-OES was developed to measure in real time the variation of the relative concentration of HM in exhaust gases.

Then, a two-phase flow bubbling bed model was developed and validated to calculate the kinetics of vaporization of HM from its measured concentration time profile in the outlet gas.

The technique was first validated with model waste (metal-spiked mineral matrices), thus enabling at each time both solid sampling for measuring the HM vaporization kinetic and on-line analysis for measuring the HM concentration in the outlet gas. The inverse method was then applied to realistic artificial wastes (derived from real wastes) to identify the HM vaporization kinetics from the on-line analysis results.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Municipal solid waste; Incineration; Heavy metal; Emission; Inverse modeling; Rate of vaporization

1. Introduction

Municipal solid waste (MSW) incineration simultaneously reduces the waste volume (about 90%) and mass (down to about 30% of the original mass), and it generates power. By now, law strictly regulates the release of toxic metals, especially in the case of MSW incineration, and the regulation may become even stricter in the future. Therefore, the treatment of the solid and gaseous effluents containing metals is an important environmental and economical issue since this procedure is spreading. Metals in wastes are introduced into combustion chambers in many physical and chemical forms. Nevertheless, during incineration, heavy metals (HM) are only partitioned and concentrated in the various final residues (bottom ash, filter ash, and residues from the air pollution control devices) and in gaseous emissions, which may then represent potential sources of pollution (possible leaching). The HM partitioning among the various residues depends on the MSW composition, on the physico-chemical properties of the metals and/or their compounds, and on the incinerator operating conditions [1].

The recycling or the disposal of the ultimate residues, in which HM are concentrated, is problematic. The toxicity of the latter depends mainly on the HM speciation (i.e. their physical and chemical forms), and not only on their elemental composition. The final HM speciation in the residues depends heavily on the combustion environment, which is influenced by the process operating parameters, such as temperature, gas composition, and residence time [1,2].

Nomenclature

C_B concentration of metallic species in the bubble phase (mg Nm^{-3})

C_E concentration of metallic species in the emulsion phase (mg Nm^{-3})

$C_o(t)$ concentration of metallic species at the bed surface at time t (mg Nm^{-3})

C_{omax} maximum concentration of metallic species at the bed surface (mg Nm^{-3})

d_p particle diameter (m)

D_B diameter of bubbles (m)

$f(t)$ vaporization flux from solid particles at time t (s^{-1})

F_B volume fraction of the bed consisting of bubbles

H height of bed at normal fluidization (m)

K_{BE} global exchange coefficient between bubble phase and emulsion phase (s^{-1})

$q(t)$ concentration of the metal in the solid particles at time t (mg kg^{-1}) (ppmw)

q_0 initial concentration of the metal in the solid particles (mg kg^{-1}) (ppmw)

$r(t)$ mass-flow rate of vaporizing metal from reactive particles $(\text{mg s}^{-1}\,\text{kg}^{-1})$

t time (s)

U superficial gas velocity (m s^{-1})

U_{mf} minimum fluidization velocity (m s^{-1})

U_B^* bubble rise velocity (m s^{-1})

Greek letters

ε_0 void fraction of bed at static condition

ε_{mf} void fraction of bed at minimum fluidization

γ_B volume fraction of solid particles dispersed in bubbles (empirical value: 0.005)

θ volume fraction of reactive metal-spiked particles in the bed

ρ_{sand} density of sand (kg m^{-3})

ρ_p density of reactive metal-spiked particles (kg m^{-3})

Based on the literature survey, there exists no published kinetic data on the release of metals during the incineration of MSW. In most studies, the heavy metal behavior (partitioning) during incineration was either studied by direct characterization of solid residues [1,3], or it was predicted by thermodynamic equilibrium analysis [4,5]. Thus, HM behavior and fate during MSW incineration cannot be controlled in today's processes because it is not yet possible to predict at which moment, at which rate (time duration), and to which extent HM are released during incineration. Kinetic information are required to understand better the HM behavior in addition to thermodynamics. The aim of

this paper is to present an inverse method for identifying the kinetics of vaporization of a metal from experimental and theoretical investigations of the incineration of model wastes in a fluidized bed reactor. The method involves on-line measurements of metals in the exhaust gas and a model of fluidized bed.

In this study, a reactive fluidized bed model developed for unsteady state, that requires short calculation times, was used to identify the kinetics of vaporization of a metal from a model waste. Batch experiments were carried out in a high-temperature fluidized bed. They dealt with three metals of most concern (Cd, Pb, and Zn) that were selected and investigated for several reasons. First, these metals are among those most emitted in air [6]. Second, Cd, Pb, and their compounds in fumes are extremely hazardous to human health. Moreover, although Cd appears at low levels in MSW (5–15 ppmw) compared to Pb and Zn [3], it is volatilized, mostly as $CdCl_2$, and emitted as particles to a considerable extent; 99% of the vaporized Cd condenses on dust particles [7]. So, the ash enrichment factor is about 100, which influences the ultimate disposal of filter ash because of the leaching of Cd-containing species.

An on-line gas analysis system, involving inductively coupled plasma-optical emission spectroscopy (ICP-OES), was linked to a laboratory-scale fluidized bed incinerator. The gas to be analyzed was injected into an argon plasma. The analytic device was based on the spectroscopic detection of the trace elements in the gaseous phase. This system allows continuous measurement of the transient concentration of each metal in the off-gas, after the metal was released from a spiked matrix, which had previously been injected batch-wise in the hot fluidized bed. When organic matrices or real wastes are burning, the concentrations of metals in the exhaust gas are the only experimental information available, since the burning solids cannot be sampled. The kinetics of vaporization of a metal from the solid waste (at the particle level) can be obtained by applying the inverse model developed for transient conditions.

2. Experimental set-up and methods

2.1. Fluidized bed reactor

The experimental set-up is represented in Fig. 1. It involves a fluidized bed (0.105 m i.d., 0.4 m high cylinder topped by a 0.2 m disengaging height) made in AISI 316 L stainless steel, as described in detail by Abanades et al. [8,9]. The fluidized bed was electrically heated by two half-cylinder radiative shells 0.2 m high, and K-thermocouples measured the temperature at several bed heights, as well as at the inlet and outlet. The reactor was insulated by alumina–silica blocks stapled onto an aluminum shell. A data acquisition software recorded every measurement on a PC. The bed was composed of silica sand (mean diameter: 700 μm; total mass of sand bed: 1.62 kg; initial depth of packed bed: 0.15 m). Once the
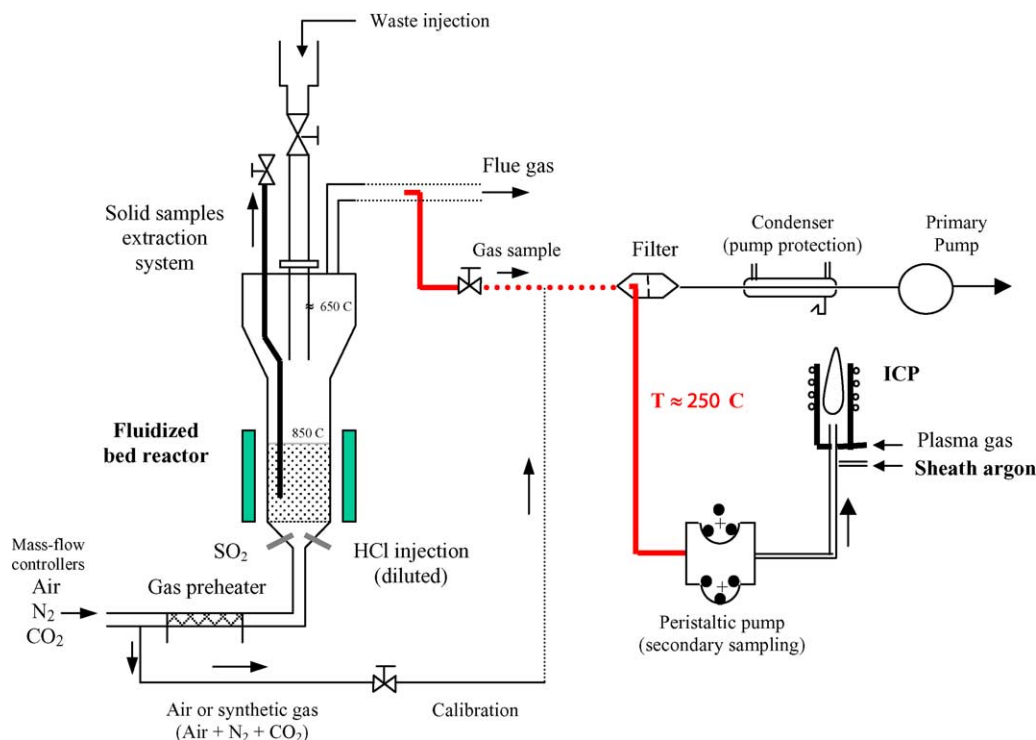
Fig. 1. Schematic of the experimental set-up.

reactor was in thermal steady state, a given mass of particles spiked with a metal was injected in the bed.

The fluidizing gas was a mixture simulating the gaseous conditions in an incinerator and it was preheated through a series of two electrical resistances. Gas flow-rates were measured by mass-flow controllers and the global composition of the synthetic gas supply was (vol.%) 4.8% O_2, 70.8% N_2, 8.8% CO_2, 400 mg Nm^{-3} SO_2, 15.6% H_2O, and 1000–2000 mg Nm^{-3} HCl. Only neutral gas passed through the electrical resistances for preheating. Both SO_2 and HCl in aqueous solution were introduced downstream of the preheater to avoid corroding it. During experiments, some of the solids were withdrawn from the bed at given times to collect a sample for chemical analysis. The metal concentration in each solid sample was measured by ICP-OES, after microwave-assisted digestion in acid. This method can be implemented only in the case of mineral matrices; it provides the evolution of a metal concentration versus time in the model waste $q(t)$. Then, the vaporization rate ($r = dq(t)/dt$) was deduced to validate the model for vaporization in a fluidized bed.

2.2. Preparation of the solid waste samples

Model wastes were prepared by impregnating a mineral matrix (porous alumina particles: $d_p = 1.6$–2 mm, $\rho_p = 1348$ kg m^{-3}, initial metal concentration q_0). Then, a more realistic artificial waste (RAW) made from real MSW was considered (composition of the RAW from ultimate analysis: 69–72% volatile matter; 6–7% moisture; 23–25% ash).

A special procedure was developed to make the particles of RAW with a density suitable for fluidization, and then to spike them with a metal. In this procedure, the waste was mixed with the heavy metal in an aqueous solution of the metal compound (e.g. $CdCl_2$, $PbCl_2$, $ZnCl_2$), sand ($d_p = 0.5$ mm, MSW/sand weight ratio = 2:1), and wallpaper glue. Then the mixture was shredded, pressed into cylindrical particles (diameter: 10 mm; length: 6–12 mm; density: 600 kg m^{-3}) with a hydraulic press, then dried in an oven to be solidified and to eliminate moisture.

The metal loading level of the matrices corresponded roughly (same order of magnitude) to that measured in real MSW except for Cd (the typical concentration ranges of Cd, Pb, and Zn in MSW are 5–12, 300–1000, and 450–2000 ppmw, respectively [3,10]). The concentration chosen for Cd was much greater than in real waste (about 500 times more) for analytical detection reasons (limits of detection of ICP analysis).

2.3. On-line gas analysis system

An on-line gas analysis system based on ICP-OES technique was developed to measure in real time the metal concentration versus time profile in the exhaust gases. This system continuously measured the emission intensity (in counts/s) of an atomic metal spectral line. This emission intensity is proportional to the concentration of the element in the gas. It quantifies the emitted radiation for a given analytical wavelength corresponding to the analyzed element (the analytical wavelengths used for detection of Cd, Pb,

and Zn were 226.50, 220.35, and 213.85 nm, respectively). This method coupled with a global fluid-bed model was used to determine the vaporization rate of the metals from burning organic matrices, i.e. without sampling the fluidized solids.

The ICP spectrometer (Jobin Yvon JY 38S), classically used for analyzing liquid samples, was adapted to allow the gas injection directly into the argon plasma [9,11,12]. The interface, consisting of two sampling stages, is schemed in Fig. 1. The gas sample to be analyzed was aspired through a primary sampler (membrane pump) and transported through a 5 m line (4 mm i.d.) that was heated to prevent any water condensation. A secondary sampler (peristaltic pump) was used to inject a low gaseous flow (100 mL/min) into the customized ICP plasma torch. The metal species were injected into the plasma torch as gaseous or as condensed microparticle droplets carried by the gas stream.

Experimental data were obtained as profiles of relative intensity, which are proportional to concentration profiles. The intensity of metal emission was measured continuously by the ICP-OES system after a batch of reactive particles had been injected into the fluidized bed in a steady state. The intensity of the signal was proportional to the concentration of metal because both the gas composition and the flow rate of sampling were constant. This method gave a good qualitative indication of the transient concentration of metal in the off-gas. The accuracy of concentration measurements depends on the plasma temperature, and the limits of detection of this method depend on the experimental conditions, on the flow-rate, and on the spectrometer itself; they can be as low as a few $\mu g\,m^{-3}$ [12]. In future work, a calibration will be required to obtain absolute concentrations of metal from the intensity measurements, since ICP spectroscopy is a comparative method.

3. Modeling of heavy metal vaporization in a bubbling fluidized bed

3.1. Objective and method

The objective of the modeling is to determine the vaporization rate of heavy metals from the solid matrix (at the particle scale), knowing only the profile of emission intensity of metallic spectral lines in the off-gas. This method is developed here for transient conditions. The procedure is as follows:

1. Develop the direct model of fluidized bed for the reaction system, and use the experimental vaporization rate ($r = dq/dt$) measured with mineral matrices as inlet parameter in the direct model, in order to calculate the concentration of heavy metal in the outlet gas (C_o).
2. Develop an inverse model that permits the calculation, for any kind of matrix, of the metal vaporization rate (r) from the metal concentration profile in the outlet gas (C_o).

3. Set the inverse model in dimensionless form to determine the dimensionless flux of vaporization $f\,(s^{-1})$ that is related to r. It consists in identifying f from the normalized profile of concentration (C_o/C_{omax}), which is equal to the normalized profile of emission intensity (I/I_{max}) for a given wavelength.
4. Validate the inverse model with the results from mineral matrix (i.e. compare the model results with the experimental measurements). In the case of mineral matrices, the metal vaporization rate ($r = dq/dt$) can be determined experimentally by analyzing solid samples withdrawn from the bed. These rates were compared with the theoretical ones predicted by the inverse model from the normalized intensity profile (I/I_{max}), in order to validate the method.
5. Apply the method to realistic artificial wastes spiked with heavy metals to predict the rate of vaporization from the measured concentrations in outlet gas.

3.2. Direct modeling

A modified version of Kunii and Levenspiel's model [13] was developed to treat beds of Geldart group B particles in which large clouds can be formed containing the main part of the solid. This model has been adapted here to the vaporization of heavy metals from solid waste.

The main assumptions of the model are the following:

- The bed is composed of two phases: the bubbles containing a small amount of solid, and the emulsion-clouds phase, corresponding to the rest of the bed.
- Bubbles have a uniform diameter.
- The gas flow in the emulsion phase is at minimum fluidization.
- The gas is in plug flow in each phase.
- There is a mass transfer between both phases, and the global mass transfer coefficient is estimated from the relation [14]:

$$K_{BE} = 4.5\frac{U_{mf}}{D_B} \tag{1}$$

- The fluidized bed is isothermal.
- The variations of the volumetric gas flow-rate due to chemical and physical conversions are negligible. Indeed, the HM vaporization flux is weak compared to the fluidization gas flow. Moreover, when dealing with organic matrices, the resulting combustion gas flow does not affect significantly the global gas flow-rate, since the sample mass injected into the bed represents less than 1% of the total bed mass.
- The gas velocity (U) is supposed to be constant in the bed.

Hence, the internal phenomena that take place within solid particles (heat and mass transfer, chemical reactions) have no effect on the results. This macroscopic approach uses only the global generation flux of metallic species at the external surface of the particles. The main advantage is that parameters
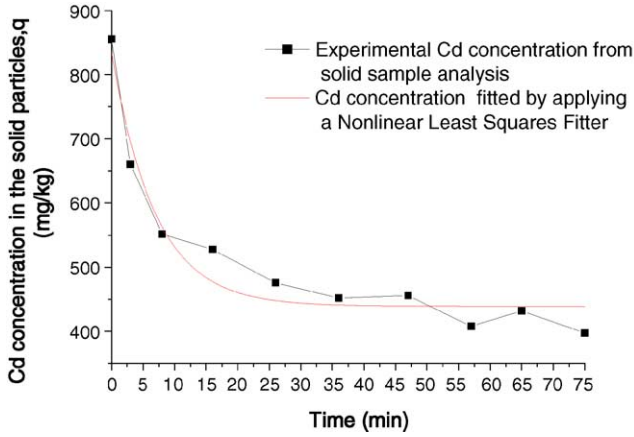
Fig. 2. Cd concentration in the alumina particles vs. time at 850 °C (130 g of alumina, $q_0 = 856$ ppmw, $C_{HCl} = 1374$ mg Nm^{-3}).

such as the physical and chemical properties of the metallic compounds or the nature of the burning waste are not required in this global two-phase flow fluid-bed model. The direct model predicts the concentration of a metal species i in the bubble phase (C_B) and in the emulsion-clouds phase (C_E) as a function of bed height (h), by solving the following mass balances for both phases (written for an elemental height step $[h, h + dh]$):

Bubble phase:

$$-F_B \left(U_B^* \frac{\partial C_{Bi}}{\partial h} + \frac{\partial C_{Bi}}{\partial t} \right)$$
$$= -F_B \gamma_B \theta r \rho_p + F_B K_{BE}(C_{Bi} - C_{Ei})$$
$$+ F_B \gamma_B (\rho_p \theta v_{spiked} + \rho_{sand}(1 - \theta)v_{sand}) \qquad (2)$$

Emulsion-clouds phase:

$$-(1 - F_B) \left(U_{mf} \frac{\partial C_{Ei}}{\partial h} + \frac{\partial C_{Ei}}{\partial t} \right)$$
$$= -(1 - F_B)(1 - \varepsilon_{mf})\theta r \rho_p - F_B K_{BE}(C_{Bi} - C_{Ei})$$
$$+ (1 - F_B)(1 - \varepsilon_{mf})(\rho_p \theta v_{spiked} + \rho_{sand}(1 - \theta)v_{sand})$$
$$(3)$$

These general equations take into account the phenomena of adsorption and condensation of metals on particles. v_{spiked} and v_{sand} denote the adsorption uptake rates on reactive particles and sand, respectively (mg s^{-1} kg^{-1}). Actually, these terms are neglected because of the lack of sorption data.

3.2.1. Simulation in the case of an alumina matrix

It was found experimentally that the metallic chloride CdCl$_2$ vaporized rapidly in the first moments. Then, the binary oxide (CdO·Al$_2$O$_3$) was formed, which inhibited Cd vaporization, and the final percentage of Cd vaporization was about 55%. Fig. 2 represents the Cd concentration versus time profile $q(t)$ in alumina particles determined by solid sampling.
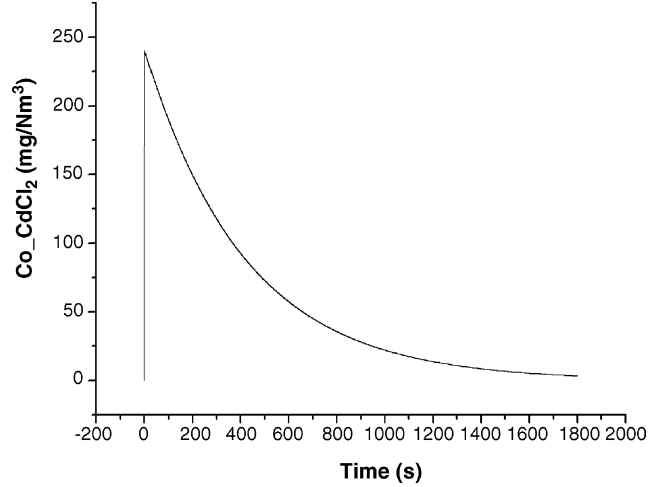

Fig. 3. Simulation (direct model): CdCl$_2$ concentration in the exhaust gas vs. time at 850 °C.

The experimental rate profile r ($= dq/dt$) of Cd vaporizing from intermittently sampled alumina particles was used as inlet data in the direct model. Finally, the direct model determined the time course of the metal species concentration in the gas $C_o(t)$, as shown in Fig. 3. The result of this simulation is that the concentration of CdCl$_2$ in the exhaust gas increases sharply from zero to a maximum in a few seconds. Then, it decreases with time and tends to zero.

3.3. Development of the inverse model

The inverse model is intended to predict the rate of metal vaporization, knowing its concentration in the outlet gas. So, the rate of metal vaporization can be determined for burning matrix. On-line analysis gives the profile of emission intensity versus time, which can be normalized (I/I_{max}). It is the same as that of concentration ($C_o^* = C_o/C_{omax}$), since intensity and concentration are proportional. Then, the inverse model calculates the dimensionless flux of vaporization f (s^{-1}) from the relative outlet concentration (C_o/C_{omax}).

The model equations (Eqs. (2) and (3)) in transient state (unsteady conditions) can be written in dimensionless form as (the terms of metal uptake by the bed particles are neglected):

$$\frac{\partial C_B^*}{\partial h} + \frac{1}{U_B^*}\frac{\partial C_B^*}{\partial t} = \frac{f}{U_B^*} - \frac{K_{BE}}{U_B^*}(C_B^* - C_E^*) \qquad (4)$$

$$\frac{\partial C_E^*}{\partial h} + \frac{1}{U_{mf}}\frac{\partial C_E^*}{\partial t} = (1 - \varepsilon_{mf})\frac{f}{\gamma_B U_{mf}}$$
$$+ \frac{F_B}{1 - F_B}\frac{K_{BE}}{U_{mf}}(C_B^* - C_E^*) \qquad (5)$$

The dimensionless flux of vaporization f (s^{-1}), which is related to the mass-flow rate of vaporization r (mg kg^{-1} s^{-1}), is expressed as:

$$f = \frac{\gamma_B \theta \, r \rho_p}{C_{omax}/F_B} \qquad (6)$$

The outlet metal concentration is given by:

$$C_o^* = \left[C_B^* + \frac{(1 - F_B)}{F_B} C_E^* \right]_{h=H} \quad (7)$$

where the dimensionless concentrations C_E^* and C_B^* are defined as:

$$C_E^* = \frac{C_E}{C_{omax}/F_B}, \quad C_B^* = \frac{C_B}{C_{omax}/F_B} \quad (8)$$

As boundary conditions, C_E^* and C_B^* are nil at the distributor level ($h = 0$). At initial time ($t = 0$), C_E^* and C_B^* are nil too in the whole bed, as well as the rate of vaporization r ($= dq/dt$).

The relative concentration at the outlet (C_o^*) is known from experiment and the aim of the inverse method is to deduce the flux of vaporization (f) from burning waste at each time t. A temporal discretization in Eqs. (4) and (5) leads to a system of two ordinary first-order differential equations, which can be solved by Runge–Kutta–Fehlberg's method using the unsettled step technique [15]. An iterative process on f is used at each time t; after initializing f, C_E^* and C_B^* are calculated for each height by solving Eqs. (4) and (5), and then C_o^* is deduced from Eq. (7). If the value of the calculated C_o^* is different from the real value (which is known from experiment), then f is incremented and C_o^* is calculated again until the real value is reached. The same iterative process is used for each time. Thus, with this inverse method, the time evolution of the flux of vaporization f can be determined from the concentration profile (C_o^*) measured at the outlet of the process.

4. Rate of metal vaporization from on-line measurements

4.1. Method validation: case of alumina matrix

4.1.1. Experimental results

The net emission intensity I_{net} (i.e. after withdrawing the background intensity) of spectral lines of metal was measured on-line versus time. Whatever the matrix, the metal concentration in gas exhibited a peak almost instantaneously after the reacting sample was injected into the fluidized bed [9].

Fig. 4 plots the kinetics of Cd vaporization relative to alumina particles ($r = dq/dt$) and to the gas phase. These plots were obtained independently from the curves of the metal concentration in alumina $q(t)$ (shown in Fig. 2), and of the emission intensity of a given characteristic peak of Cd (emission wavelength at 226.50 nm). On-line analysis of the gas was performed every 2 min. ICP measurement showed a sharp increase in the metal concentration in gas (right ordinate) when the Cd rate of vaporization (left ordinate) was maximal, with a 3–4 min lag due to both the ICP measurement technique and to the length of the sampling line. At times over about 16 min, Cd in the gas was not detected any more (the emission intensity decreased to zero) because its rate of vaporization was too low.
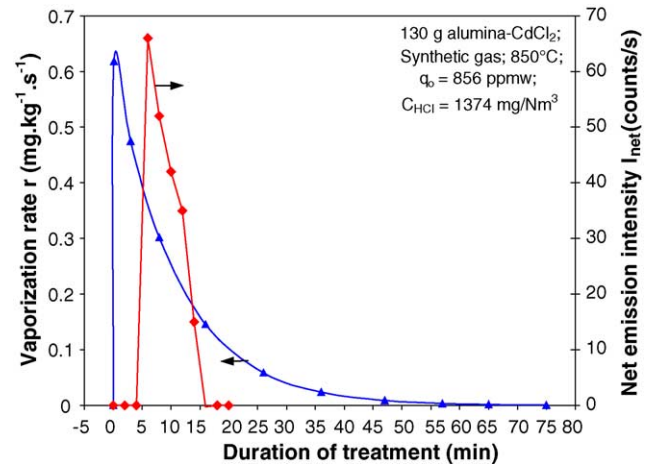

Fig. 4. Experimental Cd vaporization rate (r) from alumina, and emission intensity of its wavelength vs. time.

4.1.2. Inverse method

From the fit of the normalized intensity profile (I/I_{max}) of Cd spectral line (I shown in Fig. 4), the flux of vaporization of Cd (from porous alumina particles) was determined by applying the inverse model. Fig. 5 plots the comparison between this calculated flux of vaporization and the experimental values obtained from the analysis of solid samples.

The theoretical profile of flux of vaporization is clearly consistent with the experimental results. The discrepancy between the calculated flux and the experimental flux is about 11% in the first moments, and it decreases with time. This statement can be explained if an important point is reminded: an uncertainty on the experimental metal concentration profile in alumina $q(t)$ exists in the first moments because: (1) $q(t)$ decreases sharply in the first moments; (2) the rate of vaporization r ($= dq/dt$) is nil at initial time. To calculate the experimental vaporization flux f, the concentration of metal in the solid $q(t)$ was measured first (by solid sampling), and
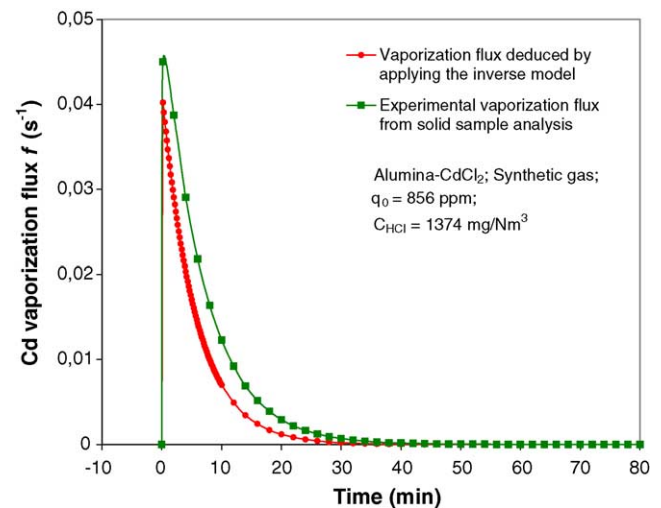

Fig. 5. Comparison between the Cd vaporization flux (f) obtained from the inverse model and the experimental one.
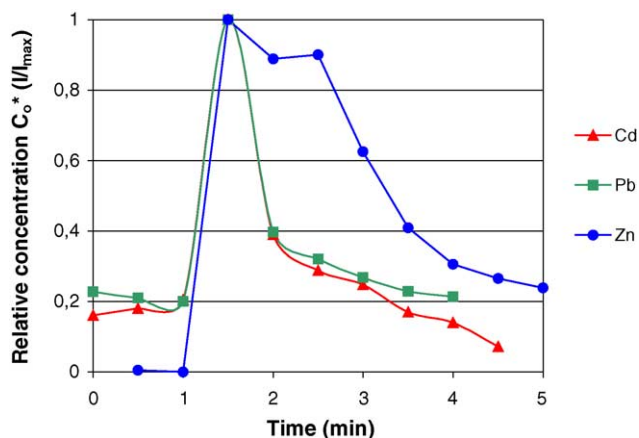
Fig. 6. Experimental profile of relative concentration of Cd ($q_0 = 4160$ ppmw), Pb ($q_0 = 2980$ ppmw), and Zn ($q_0 = 2700$ ppmw) from on-line analysis vs. duration of treatment (10 g of RAW sample in each run; synthetic gas without HCl; 850 °C).

a fit was then applied to $q(t)$ to calculate $r(t)$ which is related to f (by Eq. (6)). Nevertheless, the experimental results were in good agreement with the model predictions.

Thus, the results from on-line gas analysis can be used to estimate the rate of vaporization of heavy metals by applying the inverse model.

4.2. Case of realistic artificial waste

For realistic artificial waste made from real MSW, thus containing organic species, the profiles of vaporization of metals in the exhaust gas are the only data available. Fig. 6 represents the normalized intensity profiles (i.e. relative gaseous concentrations) of the three metals Cd, Pb, and Zn. They were fitted for time <1.5 min and time >1.5 min.

For each metal, the vaporization rates from the solid (represented in Fig. 7) were obtained by applying the inverse
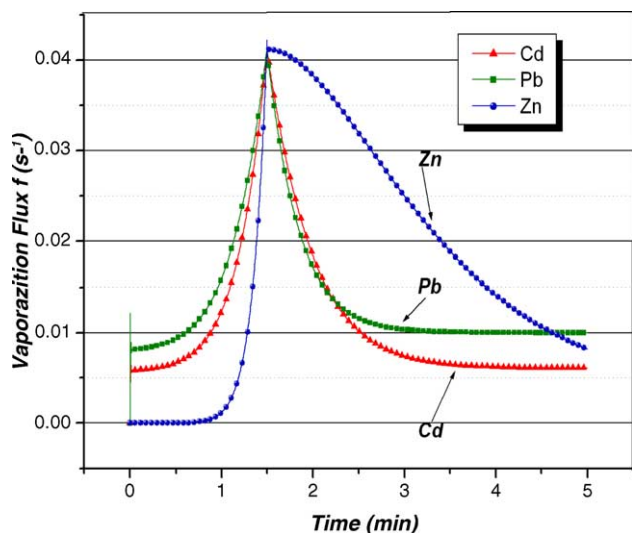

Fig. 7. Results of inverse model: time course of the vaporization flux of metal (*f*) from the RAW.

model to the experimental data. The vaporization of Zn from the burning waste is less rapid than that of Cd and Pb. Zn may be stabilized as alumino-silicates compounds in the matrix, which could inhibit its vaporization [2].

This method leads to discretized results. The on-line analysis system, once an appropriate calibration device is implemented, will permit the measurement of quantitative data on trace elements in combustion gases. Actually, the bed of sand may adsorb a small amount of the heavy metal vaporized. Hence, the model will have to take into account the metal uptake by the bed material when dealing with quantitative data (i.e. variation of absolute concentration).

By integrating the rate of vaporization ($r = \mathrm{d}q/\mathrm{d}t$) obtained from the inverse method, the time course of the HM concentration in the solid waste $q(t)$ will be assessed. The advantage is that a kinetic law can be deduced from the relation between the rate of vaporization $r(t)$ and the metal concentration in the solid $q(t)$. The inverse method that features a macroscopic approach allows to identify global kinetics of HM release. In future work, a particle-scale model (based for instance on a shrinking-core model or on a decreasing particle size model) will be developed accounting for combustion phenomena and HM vaporization. Such a model was developed previously in the case of HM vaporization from mineral porous matrices [16]. The intrinsic kinetics of HM release obtained with a particle-scale model will have to be compared with the global kinetics from the inverse method.

Finally, the on-line diagnostic technique, tested successfully on realistic artificial waste, will be useful for both laboratory studies and industrial process control of HM release, and whatever the type of burner or incinerator. Moreover, the same global method can be applied in incineration processes to determine the rate of formation of any pollutant, from the measurement of its concentration in off-gas.

5. Conclusion

A global method was developed to determine the rate of vaporization of metal from the on-line analysis of exhaust gas of incinerator burning real wastes. It is an inverse method, that was developed and tested by determining the rate of vaporization from the analysis of the exhaust gas in the case of realistic matrices derived from real wastes. It involves an on-line system of gas analysis, based on ICP spectrometry, which is coupled to the gas outlet of the reactor, and an inverse model that was developed at the reactor scale. This procedure was first validated with model wastes, based on mineral matrices spiked with metal. It was then applied to realistic artificial wastes made from real wastes. Whatever the matrix and the metal, the kinetics of metal vaporization were deduced from the on-line analysis results by applying the inverse model. Then, kinetic laws could be determined from these profiles of rate of vaporization.

This inverse method, which involves only an on-line analysis of exhaust gases and a model developed at the reactor

scale, could be implemented to incineration processes to identify the kinetics of release of any pollutant.

References

[1] P.H. Brunner, H. Monch, The flux of metals through municipal solid waste incinerators, Waste Manag. Res. 4 (1986) 105–119.

[2] W.P. Linak, J.O.L. Wendt, Toxic metal emissions from incineration: mechanisms and control, Prog. Energy Combust. Sci. 19 (1993) 145–185.

[3] A.J. Chandler, T.T. Eighmy, J. Hartlén, O. Hjelmar, D.S. Kosson, S.E. Sawell, H.A. van der Sloot, J. Vehlow, Municipal solid waste incinerator residues, in: The International Ash Working Group (IAWG), Elsevier Science, Amsterdam, 1997.

[4] S. Abanades, G. Flamant, B. Gagnepain, D. Gauthier, Fate of heavy metals during municipal solid waste incineration, Waste Manag. Res. 20 (1) (2002) 55–68.

[5] F. Frandsen, K. Dam-Johansen, P. Rasmussen, Trace elements from combustion and gasification of coal—An equilibrium approach, Prog. Energy Combust. Sci. 20 (1994) 115–138.

[6] CITEPA (Centre Interprofessionnel Technique d'Etudes de la pollution Atmosphérique), Emissions dans l'air en France: métaux lourds, 2001, 20 pp.

[7] H. Vogg, H. Braun, M. Metzer, J. Schneider, The specific role of cadmium and mercury in municipal solid waste incineration, Waste Manag. Res. 4 (1986) 65–74.

[8] S. Abanades, G. Flamant, D. Gauthier, Kinetics of heavy metal vaporization from model wastes in fluidized bed, Environ. Sci. Technol. 36 (17) (2002) 3879–3884.

[9] S. Abanades, D. Gauthier, G. Flamant, C. Trassy, On-line heavy metal analysis in the fumes from a laboratory fluid bed incinerator, Combust. Sci. Technol. 175 (4) (2003) 759–774.

[10] J.Y. Le Goux, C. Le Douce, L'incinération des déchets ménagers, Economica, 1995, 226 pp.

[11] C. Trassy, R. Diemiaszonek, Heavy elements in gaseous effluents: study of an on-line analytical method, High Temp. Chem. Process. 3 (4) (1994) 449–458.

[12] S. Hassaine, C. Trassy, P. Proulx, Continuous emission monitoring of metals in flue gases by ICP-OES: role of calibration and sample gas High Temp, Mater. Process. 5 (2001) 313–331.

[13] D. Kunii, O. Levenspiel, Fluidization Engineering, second ed., Butterwort-Heinemann, Boston, 1991.

[14] B. Caussat, M. Hemati, J.P. Couderc, Modélisation des réacteurs à lit fluidisé gaz-solide: prise en compte de la variation du débit gazeux due aux réactions chimiques, Chem. Eng. J. 58 (1995) 223–237.

[15] E. Hairer, S.P. Norsett, G. Wanner, Solving Ordinary Differential Equations, Nonstiff Problems, vol. 1, second ed., Springer, Berlin, 1993.

[16] S. Abanades, G. Flamant, D. Gauthier, Modeling of heavy metal vaporization from a mineral matrix, J. Hazard. Mater. 88 (1) (2001) 75–94.