



HAL
open science

Thermodynamic study of heavy metals behaviour during municipal waste incineration

Y. Menard, A. Asthana, F. Patisson, P. Sessiecq, D. Ablitzer

► **To cite this version:**

Y. Menard, A. Asthana, F. Patisson, P. Sessiecq, D. Ablitzer. Thermodynamic study of heavy metals behaviour during municipal waste incineration. *Trans. IChemE, Part B, Process Safety and Environmental Protection*, 2006, 84, pp.290-296. 10.1205/psep.05166 . hal-00124955

HAL Id: hal-00124955

<https://hal.science/hal-00124955>

Submitted on 17 Jan 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THERMODYNAMIC STUDY OF HEAVY METALS BEHAVIOUR DURING MUNICIPAL WASTE INCINERATION

Y. MÉNARD, A. ASTHANA, F. PATISSON, Ph. SESSIECQ* and D. ABLITZER

Laboratoire de Science et Génie des Matériaux et de Métallurgie (LSG2M) Nancy, France

The incineration of municipal solid waste (MSW) contributes significantly to the presence of heavy metals in urban area aerosols. It is thus important to ascertain the quantities and chemical forms of the heavy metals (HM) that are emitted from the incineration plant stacks. The behaviour of HM, which depends strongly on the thermal and chemical environments, was investigated herein with a modelling approach, consisting of several parts. First, a refuse bed combustion model was developed for simulating on-grate MSW incineration. It describes most of the physico-chemical and thermal phenomena occurring during waste combustion. Second, results from the bed model were taken as boundary conditions to perform 3D simulations of the post-combustion zone and of the boiler. The case studied was of the Strasbourg incineration plant. Finally, the local thermal conditions and the local elementary compositions of gas and solid phases obtained from these simulations were used to carry out thermodynamic calculations of the speciation of HM at each point in the incinerator. The results for four metals (Cd, Zn, Pb, Cr) are presented, discussed and compared to available data. Predicted species are in agreement with observations for volatile metals, except lead, whose volatilization seems overestimated.

Keywords: heavy metals, municipal waste, incineration, simulation, thermodynamics.

INTRODUCTION

The objective of this study is to predict the behaviour of heavy metals contained in the municipal wastes during their incineration in a grate furnace. Considering the diversity and the complexity of the physical phenomena involved during the transformation of the heavy metals in a MSW incineration unit, it is essential to understand the behaviour of these heavy metals in detail. It is important to know at each point in the incinerator the physico-chemical and thermal conditions (temperature, gas concentration, residence time, gas velocity, and so on), which govern the transformation of the metal species. This holds as well in the layer of the solid wastes undergoing combustion on the grate, in the post-combustion chamber and in the boiler zone. These local conditions are poorly known in an industrial unit: they cannot be measured locally and the results obtained from macroscopic balances are not sufficient for giving a detailed realistic description of the combustion process. Thus, the approach we adopted is to determine these local conditions from simulations. The results of these simulations, when coupled with thermodynamic equilibrium calculations, give an interesting insight into the heavy metals behaviour in the incineration process.

The first part of this paper describes the modelling and simulation of the on-grate MSW combustion. The second part is dedicated to the study of the specific behaviour of four heavy metals by thermodynamic equilibrium calculations making use the results obtained from the simulations.

COMBUSTION OF A BED OF MSW MOVING ON THE GRATE OF AN INCINERATOR

We have developed a new mathematical model for simulating the behaviour of a burning MSW bed (Ménard, 2003). This model describes most of the physico-chemical and thermal phenomena occurring during waste combustion like gas flow, heat and mass transfer, drying, pyrolysis, combustion of pyrolysis gases, combustion and gasification of char, and bed shrinkage. The model is based on the following assumptions:

- The bed of MSW is a porous medium of varying height and is made up of spherical particles of solid waste. The solid moves with the grate and a gas flows across (primary air + products from the bed degradation).
- Gas and solid temperatures are different.
- The refuse feed consists of an inert part, a pyrolysable part (which itself is composed of different fuels like plastics, paper, cardboard, textiles) leaving a carbonaceous residue (char) after devolatilization, and water.

*Correspondence to: Dr Ph. Sessiecq, LSG2M, Ecole des Mines de Nancy, Parc de Saurupt, 54042 Nancy Cedex, France.
E-mail: sessiecq@mines.inpl-nancy.fr

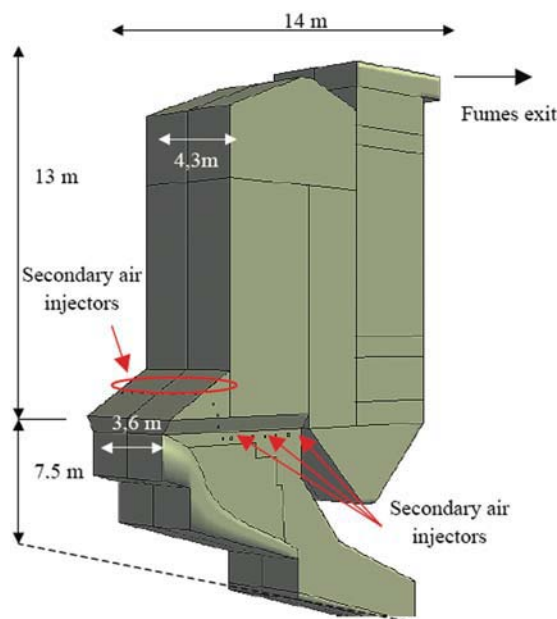


Figure 2. Diagram of the incinerator of Strasbourg.

Speciation of Heavy Metals in the Burning MSW Bed

For the thermodynamic calculations in the MSW bed, it is necessary to identify the chemical elements that constitute the system under study. Thus, 29 chemical elements were retained for the purpose of calculations: C, H, O, N, S, Cl and F represent the organic phase and the air of combustion; Si, Ca, Mg, Na, K, Al, Fe, P, Mn and Ti represent the mineral phase (slag + ashes) with their oxides (SiO_2 , CaO , MgO , Na_2O , K_2O , Al_2O_3 , Fe_2O_3 , P_2O_5 , MnO and TiO_2); and Cr, Zn, Pb, Cd, Hg, B, Cu, Ni, Co, As, Ba and Sn represent the heavy metals or trace elements present in the MSW. From these 29 elements, 1772 chemical species under condensed or gaseous form were identified in the thermo-chemical data-bank of GEMINI.

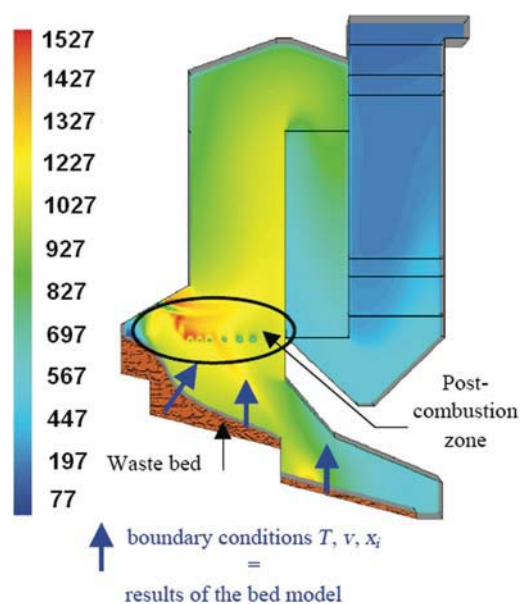


Figure 3. Temperature map in °C, from Menard (2003).

To avoid treating the whole bed of wastes in the calculations, three heights in the feed were selected (Figure 4): the elementary volumes situated on the surface of the charge, those at mid-height and those situated at a height of approximately 3 cm above the grate. The elementary composition of these local systems, which are input data for the thermodynamic calculations, are calculated from the mass flow rates (gas and solid) entering in each elementary volume, known from the bed model calculations. Thus, the thermodynamic calculations at each grid-point are independent of the thermodynamic calculations at the neighbouring points. The evolution of these compositions is directly linked to the evolution of the local composition of the solids (water content, residual carbon content, presence of organic constituents) and to the composition of the gas phase (oxidising or reducing medium, presence of chlorine, and so on), which traverses these volumes. Most of the flow rates are obtained from the MSW bed combustion model described previously. The chlorine and sulphur concentrations are not directly given by the bed model. They are calculated from the mass fractions of these elements in the feed. It is assumed that chlorine and sulphur leave the solid bed during pyrolysis, proportionally to the pyrolysis rate. With this description, the elementary volumes situated under the pyrolysis front do not contain chlorine or sulphur except in the solid phase, their concentrations being equal to their initial concentrations. The elementary volumes situated above the pyrolysis front have null or negligible chlorine and sulphur concentrations in the solid phase as these have almost completely passed into the gas phase during pyrolysis. The quantities of heavy metals in each volume are taken equal to those in the feed. Once these compositions are known, the thermodynamic calculations are systematically carried out in all selected volumes. This provides a cartography of the speciation of each metal during the combustion in the MSW bed.

Figure 5 synthesizes the results of the thermodynamic calculations for the four metals considered. It presents, at selected locations, the different forms of these metals: chemical species, molar fractions of the metals in the different species, and phases. For cadmium, this figure shows that up to the drying front, the thermodynamically stable chemical form of cadmium is the sulphide $\text{CdS}(s)$ and then the chloride $\text{CdCl}_2(s)$. Above the combustion front, stable cadmium is found in the vapour form $\text{Cd}(g)$ due to high temperatures of the bed throughout this zone. Beyond the pyrolysis front, the absence of available chlorine leads to favour the formation of $\text{Cd}(g)$. The silicate form CdSiO_3 is predicted to be the most stable species during the cooling of the ash. These results call for a few comments. They do not mean, for example, that all cadmium is found in the form of silicate in the bottom ash. Rather these are thermodynamic calculations and silicate is the stable form in this zone. The most significant result concerns the volatilisation: the large extent of the stability zone of $\text{Cd}(g)$ (over the whole height of the bed) implies that cadmium will indeed entirely vaporize and leave the bed as metal vapour $\text{Cd}(g)$ and, in smaller quantity, as chloride $\text{CdCl}_2(g)$.

The chemistry of lead is more complex than that of cadmium. At the entrance of the grate, the stable form of lead is the solid sulphide PbS (melting point = 1113°C).

streamlines starting from the bed surface at abscissas 0.5, 4, 8 and 11 m.

In the current state of our FLUENT model, some species are not directly handled and their concentrations in the gas have to be evaluated separately. Thus, chlorine and sulphur concentrations are calculated from the average equivalent concentration of HCl (600 mg Nm^{-3}) and of SO_2 (70 mg Nm^{-3}) measured in the fumes (flow rate: $65\,000 \text{ Nm}^3 \text{ h}^{-1}$) of the incineration unit of Strasbourg at the exit of the boiler, just before the gas treatment system. It is assumed that these elements are not captured in the furnace, but only downstream, in filters and in the gas treatment system, as indicated by (Le Goux and Le Douce 1995) and (Brunner and Mönch 1986). For the four heavy metals considered, the concentrations in the gas are calculated assuming a given fraction vaporized from the bed: 40% for Pb, 82% for Cd, 50% for Zn and 10% for Cr, in agreement with the same authors. Another assumption is that the mineral part of the feed

remains on the grate and does not participate in the chemical equilibrium in the gas chamber. The main thermodynamic results concerning the furnace are gathered in Figure 6.

Above the hot region of the MSW bed, cadmium is successively found in the elementary form $\text{Cd}(\text{g})$ and then as chloride $\text{CdCl}_2(\text{g})$ over the hottest part of the combustion zone. Above the last few meters of the grate the oxide $\text{CdO}(\text{s})$ is the stable species. The metallic vapours of Cd, which are transported in the fumes, become unstable and are expected to be transformed exclusively into chloride $\text{CdCl}_2(\text{g})$. Due to the cooling down of the gas in the heat exchanger, the solid sulphate CdSO_4 appears thermodynamically the most stable form at the exit of the boiler. In practice, all of the gaseous species mentioned above can condense at various places, for instance at the surface of particles transported in the fumes, and thus Cd and CdCl_2 are as likely to be found in the ashes under the boiler or filters as CdSO_4 .

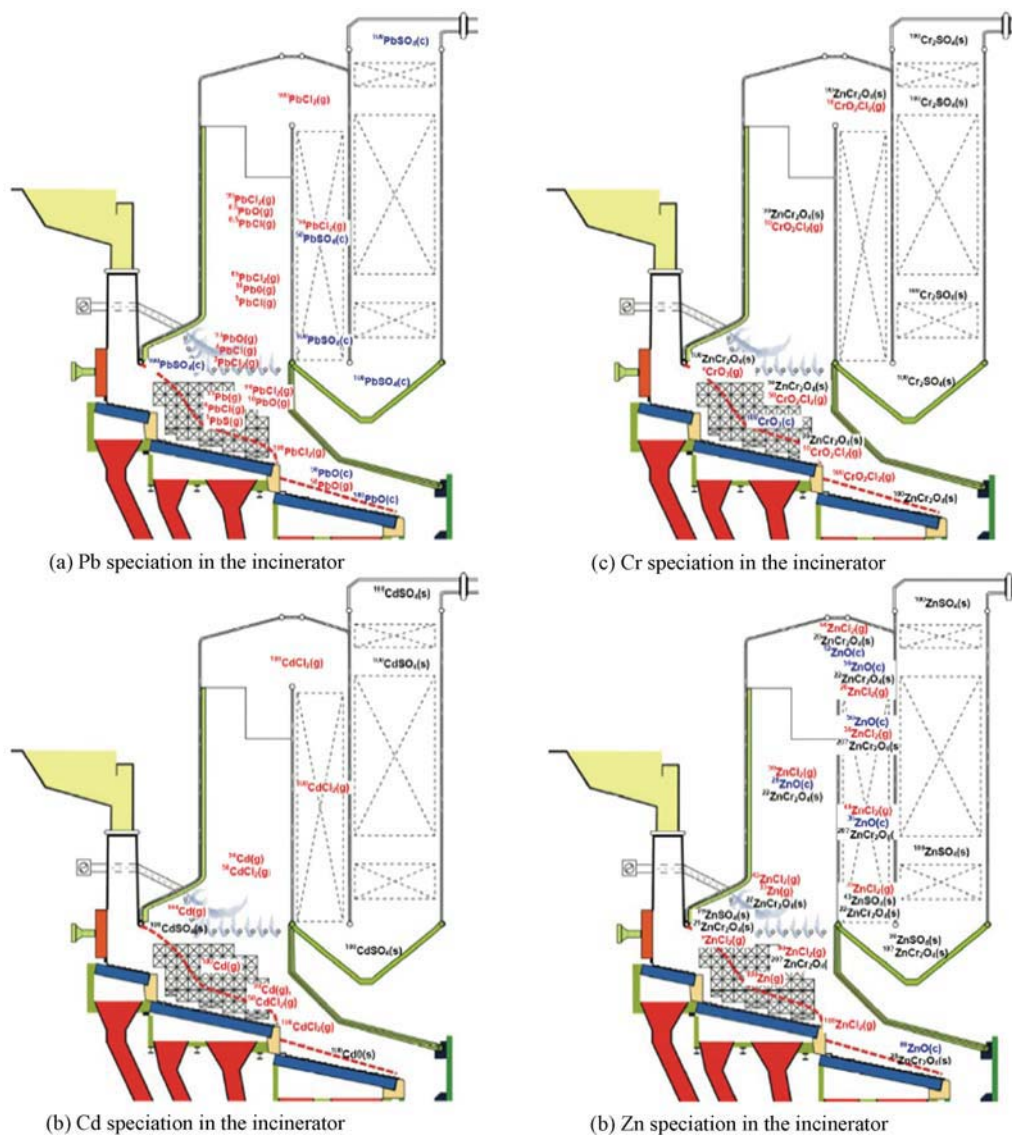


Figure 6. Heavy metal speciation in the incinerator. (s) = solid phase, (c) = condensed phase (solid or liquid), (g) = gaseous phase. The left exponent figure indicates the molar percentage of the metal found in that species at equilibrium.

Table 2. Results of speciation for the four heavy metals: Pb, Cd, Cr and Zn.

	Bottom ash	Bed surface	Boiler and filter ashes
Pb	Pb ₂ B ₂ O ₄ (s), Pb(s)	Pb(g), PbS(g), PbO(g)	PbSO ₄ (s), PbCl ₂ (s), PbO(s), Pb(s)
Cd	CdSiO ₂ (s)	Cd(g), CdCl ₂ (g)	CdSO ₄ (s), CdCl ₂ (s), Cd(s)
Cr	Na ₂ CrO ₄ (s), BaCrO ₄ (s), ZnCr ₂ O ₄ (s)	FeCr ₂ O ₄ (s), ZnCr ₂ O ₄ (s)	Cr ₂ SO ₄ (s), CrO ₂ Cl ₂ (s), ZnCr ₂ O ₄ (s), Cr ₂ O ₃ (s)
Zn	Zn ₂ SiO ₄ (s), ZnFe ₂ O ₄ (s), ZnCr ₂ O ₄ (s), ZnAl ₂ O ₄ (s)	Zn(g), ZnCl ₂ (g)	ZnSO ₄ (s), ZnCr ₂ O ₄ (s), ZnCl ₂ (s), ZnO(s), Zn(s)

As in the case of cadmium, the sulphate of lead also appears in the region situated in the proximity of the hopper at the entrance of the MSW in the incinerator. In the zone of live combustion, the principal stable species are Pb(g) and PbCl₂(g). Small quantities of PbCl(g), PbS(g) and PbO(g) are also found. PbO appears in the solid form in the last few metres of the grate and its presence in the liquid form is predicted above the char oxidation zone, where temperature exceeds the melting point of PbO (887°C). In the post-combustion chamber, lead oxide is progressively replaced by the chloride PbCl₂(g) and then by the sulphate PbSO₄(s). The species likely to be present in the ashes under the boiler and under the filters are, therefore, the sulphate and all the species mentioned above as gaseous.

From Figure 5, zinc appears to be less volatile than the two previous metals. It leaves the bed in the form of Zn(g) and ZnCl₂(g). In the post-combustion chamber, Zn(g) disappears and three stable forms appear: ZnCl₂(g) and the solids ZnO and ZnCr₂O₄. Due to the fall of the temperature in the boiler, ZnO(s) and ZnCl₂(g) are further replaced by the solid sulphate ZnSO₄. The ashes should finally contain these different forms of zinc, ZnCl₂, ZnSO₄ and ZnO.

Chromium, if some is released from the bed, is stable as gaseous CrO₂Cl₂, solid Cr₂O₃ and ZnCr₂O₄. The oxychloride form disappears in the boiler zone. The final stable species are ZnCr₂O₄(s) and then Cr₂SO₄(s).

Table 2 summarizes the main species predicted from our thermodynamic calculations.

Comparison of the Results of Thermodynamic Calculations to the Experimental Analysis

Concerning cadmium, the thermodynamic results for the burning MSW bed predict cadmium vaporization in its elementary form or as chloride CdCl₂ in the whole hot zone of the bed. This indicates a significant volatilization of this metal, in agreement with the experimental analyses (Brunner and Mönch, 1986; Reimann, 1989; Morf *et al.*, 2000). Moreover, the initial speciation of cadmium in MSW consists of easily volatile species (CdS in paint additives, Cd in pigments for plastics, Cd in batteries), which favours its vaporization. The kinetic limitations should thus be insignificant and a purely thermodynamic description is well adapted.

The behaviour of lead is more complex. Our thermodynamic calculations suggest a significant vaporization of lead whereas the experimental analyses show that 60% of lead is localized in the bottom ash after combustion (Brunner and Mönch, 1986; Reimann, 1989; Morf *et al.*, 2000). Kinetic effects, and particularly diffusional limitations for mass transport, could partly explain this

difference. Moreover, the origin of lead in MSW (only 36% in combustible components, the major part being in the form of glass and massive objects, inert for combustion) like its initial speciation in the form of not very volatile oxides, PbO, PbO₂, PbCrO₄ or PbMoO₄, (Desroches-Ducarne, 1997) explains why its vaporization during combustion is less than our thermodynamic calculations predict. Zinc remains stable in the solid phase in most of the incinerator bed and under many mineral forms (ZnCr₂O₄, ZnFe₂O₄, ZnAl₂O₄, Zn₂SiO₄). The volatility of zinc is thus lower than that of lead, as observed in experiments (Brunner and Mönch, 1986; Reimann, 1989; Morf *et al.*, 2000). Thermodynamic calculations seem to represent correctly the behaviour of zinc during the combustion. Lastly, chromium remains in the solid form, irrespective of the local conditions of composition and temperature. It forms many mixed oxides, which are found in the bottom ash. These results are in agreement with the experimental observations.

Gagnepain (1998) and Eighmy *et al.* (1995), from measurements on various ashes, established the principal chemical species met in these residues: the chemical forms most probable for Pb are the pure metal form, the oxide, the sulphate, the carbonate and the silicates, present in all ashes. PbCl₂ was identified by Gagnepain in the ashes under the boiler. Eighmy *et al.* identified PbSO₄, PbCl₂, PbO and Pb in electrostatic filter ash, in agreement with our thermodynamic results. According to Gagnepain (1998), zinc appears as metal, in the form of oxides, of chlorides on the surface of dust, of sulphates, carbonates, aluminates, silicates, and as ZnCr₂O₄ in all the residues. Eighmy *et al.* (1995) identified ZnBr₂, ZnCl₂, ZnO and Zn in filter ash. All these compounds, except the carbonates, are predicted by our thermodynamic calculations. Lastly, the possible species for chromium are pure metal, the CrO₃ oxide, FeCr₂O₄ and ZnCr₂O₄ in the slag and MgCr₂O₄ (identified by Gagnepain) and PbCrO₄ (identified by Eighmy *et al.*) in the boiler ash. Thermodynamic calculations also reveal a stabilization of chromium in many mixed oxides such as FeCr₂O₄, ZnCr₂O₄, NiCr₂O₄, CoCr₂O₄ as well as the formation of Cr₂SO₄(s), Cr₂O₃(s), CrO₂Cl₂(g) and CrO₃(g).

CONCLUSION

A thermodynamic approach was used to determine the chemical speciation of four heavy metals in a MSW incinerator in real operating conditions (incinerator of Strasbourg). These thermodynamic calculations were carried out for the refuse bed and for the post-combustion and the boiler zones of the incinerator, after having determined the local thermal and chemical conditions thanks to a combustion model of our own. This approach accounts for local

variations of composition and temperature met during the processes of combustion, which makes it possible to explain the formation of chemical species that do not appear in usual, global thermodynamics calculations. For the most volatile elements (Cd, Zn and Cr), the simulations results are in good agreement with reported observations. In the case of lead, the thermodynamic approach is inadequate. It seems necessary to consider a kinetic approach. This is one of our objectives for the continuation of this work.

REFERENCES

- Abanades, S., 2001, Comportement des métaux lourds dans le procédé d'incinération des déchets ménagers, Thèse de doctorat, Université de Perpignan, France.
- Brunner, P.H. and Mönch, H., 1986, The flux of metals through municipal solid waste incinerators, *Waste Management & Research*, 4: 105–119.
- Desroches-Ducarne, E., 1997, Étude du devenir des polluants gazeux lors de l'incinération d'ordures ménagères en lit fluidisé circulant, IFP, Thèse de doctorat, Université de Haute Alsace, France.
- Eighmy, T.T., Eusden, J.D., Krzanowski, J.E., Domingo, D.S., Martin, J.R. and Erickson, P.M., 1995, Comprehensive approach toward understanding element speciation and leaching behavior in municipal solid waste incineration electrostatic precipitator ash, *Environmental Science and Technology*, 29: 629–646.
- Gagnepain, B., 1998, Spéciation des métaux lourds dans les résidus solides d'usines d'incinération d'ordures ménagères et contribution à l'interprétation des processus de vaporisation, Thèse de doctorat, Université de Perpignan, France.
- Garcia, A.N., Marcilla, A. and Font, R., 1995, Thermogravimetric kinetic study of the pyrolysis of municipal solid waste, *Thermochimica Acta*, 254: 277–304.
- Le Goux, J.Y. and Le Douce, C., 1995, L'Incinération des Déchets Ménagers (Economica, Paris, France).
- Ménard, Y., 2003, Modélisation de l'incinération sur grille d'ordures ménagères et approche thermodynamique du comportement des métaux lourds, Thèse de doctorat, Institut National Polytechnique de Lorraine, France.
- Ménard, Y., Patisson, F., Sessieq, Ph., Ablitzer, D., Merz, A. and Seifert, H., 2002, Transient combustion of municipal waste in a grate furnace: modelling and experiments, *European Conference, the Future Of Waste Management in Europe*, Strasbourg.
- Ménard, Y., Sessieq, Ph., Patisson, F. and Ablitzer, D., 2004, Mathematical modelling of municipal solid waste incineration and thermodynamic study of the behaviour of heavy metals, *REWAS Madrid September 2004*, Proceedings edited by I. Gaballah *et al.*, TMS/INASMET, Vol. 2, 1577–1586.
- Morf, L.S., Brunner, P.H. and Spaun, S., 2000, Effect of operating conditions and input variations on the partitioning of metals in a municipal solid waste incinerator, *Waste Management & Research*, 18: 4–15.
- Owens, T.M., Wu, C.Y. and Biswas, P., 1995, An equilibrium analysis for reaction of metal compounds with sorbents in high temperature systems, *Chem Eng Comm*, 133: 31–52.
- Reimann, D.O., 1989, Heavy metals in domestic refuse and their distribution in incinerator residues, *Waste Management & Research*, 7: 57–62.

ACKNOWLEDGEMENTS

We thank O. Devisme for this help in the experimental part of the laboratory work. We are grateful to our German colleagues Prof. H. Seifert and Dr J. Vehlow for their collaboration, particularly for the KLEAA experiments, and to G. Pierotti from TIRU (Paris) for the samples and the Strasbourg plant data. Lastly, we acknowledge the financial support of CNRS and ADEME.