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Thermodynamic study of heavy metals behaviour during municipal waste incineration

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Abstract

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 that are emitted from the incineration plant stacks. The behaviour of heavy metals, 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: gas flow, heat and mass transfer, drying, pyrolysis, combustion of pyrolysis gases, combustion and gasification of char. Second, results from the bed model (temperatures, gas velocities and concentrations of gaseous compounds) were taken as boundary conditions to perform 3-D simulations of the post-combustion zone and of the boiler. The case studied was of the Strasbourg (France) 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 heavy metals at each point in the incinerator. The results obtained for 4 metals (Cd, Zn, Pb, Cr) are presented, discussed and compared to available data. Predicted species are in good agreement with observations, as well as the volatility of the metals, except that of lead, which seems overestimated.

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

1. 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, etc.), 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.

2. 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 devolatilisation, and water.
- Pyrolysis is described separately for the cellulosic and non-cellulosic fractions of the combustible solids (Garcia et al., 1995). The devolatilisation kinetics of both fractions have been determined from thermogravimetry experiments (Ménard, 2003).
- Pyrolysis produces the following primary gases: CO₂, H₂O, CO, CH₄ and H₂. The last three can combust in the presence of oxygen within the bed itself.
- Char can either burn in the presence of oxygen to produce CO and CO₂ or be gasified by CO₂ and H₂O to form CO and H₂.
- Heat is transported inside the bed by radiation, convection and conduction.

This model has been validated by comparing calculated solid temperatures and gas composition with measurements from the pilot facility KLEAA of Karlsruhe (Germany) (Ménard et al., 2002, 2004).

The model was then applied to the combustion of a MSW bed moving on the grate of the incineration plant of Strasbourg (France). Thus the conditions (velocity field of the gas phase, gas and solid (Fig. 1) temperatures, concentrations of O₂, CO, CO₂, H₂O and other gaseous components) were obtained at any point inside the MSW bed, which is the origin of the heavy metals.

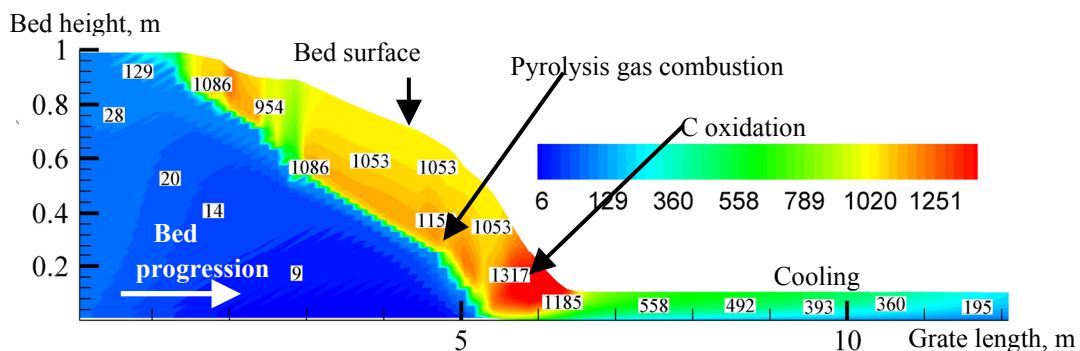


Figure 1. Solid temperature map (°C) (Flow rate = 25 000 Nm³ h⁻¹, T_{primary air} = 100°C)

Whenever the conditions are adequate for a heavy metal species to be vaporised from the bed, the vapour metal species is then transported into the post-combustion chamber and further in the boiler region. It is therefore necessary to know the thermal and chemical conditions in the whole incinerator. This is why we undertook a mathematical modelling of the gas phase of the incinerator. We used the computational fluid dynamics code FLUENT for solving the corresponding set of conservation equations for mass, momentum and energy. An original feature of our approach is that the results of the simulations of the MSW bed combustion, obtained from the bed model presented above, are used as boundary conditions (inlet) for the simulations of the post-combustion chamber and the heat exchanger of the incinerator. The latter simulations take into account the following aspects:

- Three homogeneous reactions of combustion in the gas phase, the same as those considered in the bed model, are considered.
- Turbulence is described using the “k-ε realizable” model of FLUENT, and heat exchange by the “P-1” radiation model of FLUENT.
- More than 400 000 nodes were necessary for meshing the geometry of the Strasbourg plant (Fig. 2).

These 3-D simulations are relatively time-consuming (1 to 2 weeks on workstation HP B2600) but they give access to a complete cartography of flow fields, temperatures (Fig. 3), and gas concentrations in the whole incinerator furnace.

3. Thermodynamic Study of the Behaviour of Heavy Metals in an Incinerator

The next step is the thermodynamic study of the speciation of heavy metals during the incineration of MSW. This work represents a simplified approach to predict the behaviour of the heavy metals in the process. It assumes that the chemical form in which a metal can be found at any point in the incinerator can be determined

from local thermodynamic equilibrium calculations. This is a simplification since kinetic aspects are ignored, but this is an improvement over most of the thermodynamic calculations presented in the literature (e.g. Abanades, 2001; Owens et al., 1995) that are overall calculations. We take into account the local operating conditions of the incinerator (temperature, composition in Cl, oxidising or reducing conditions, etc). This permits or forbids the formation of certain species in certain zones.

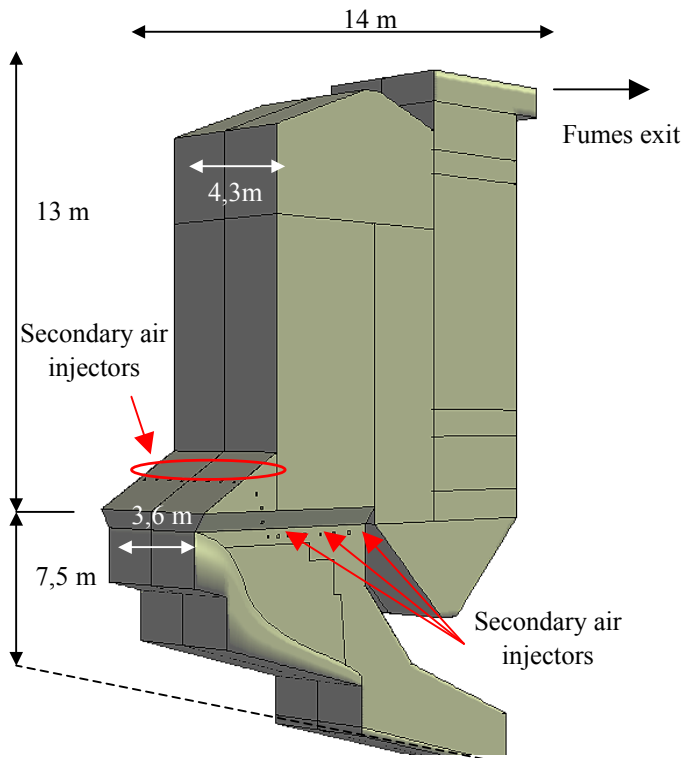


Figure 2. Diagram of the incinerator of Strasbourg

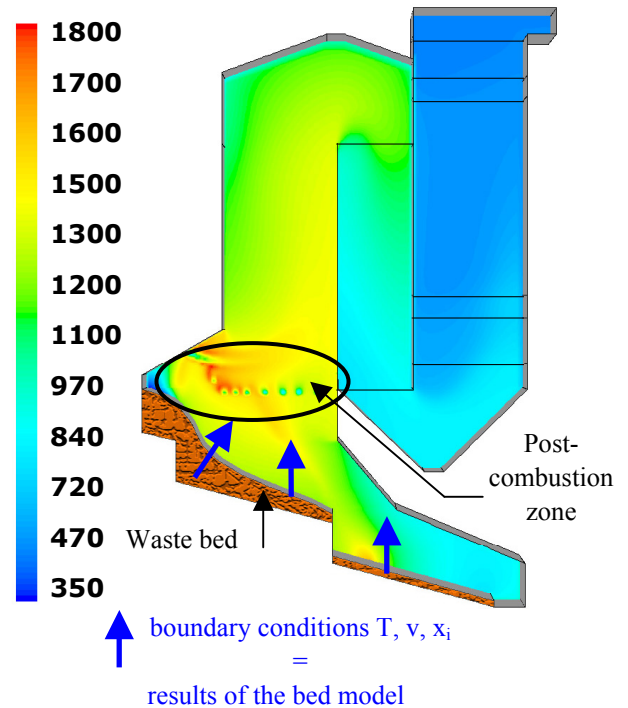


Figure 3. Temperature map, K

The thermodynamic equilibrium calculations are performed using the software GEMINI (Gibbs Energy MINImiser, developed by THERMODATA), based on the minimisation of the total Gibbs energy of a closed system under study. The results is the full composition of the system at equilibrium, i.e. the species likely to be present, their phase, and their distribution (speciation).

3.1 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.

To avoid treating the whole bed of wastes in the calculations, three heights in the feed were selected (Fig. 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, etc), which traverses these volumes. Most of the flow rates are obtained from the MSW bed combustion model described in Section 2. 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.

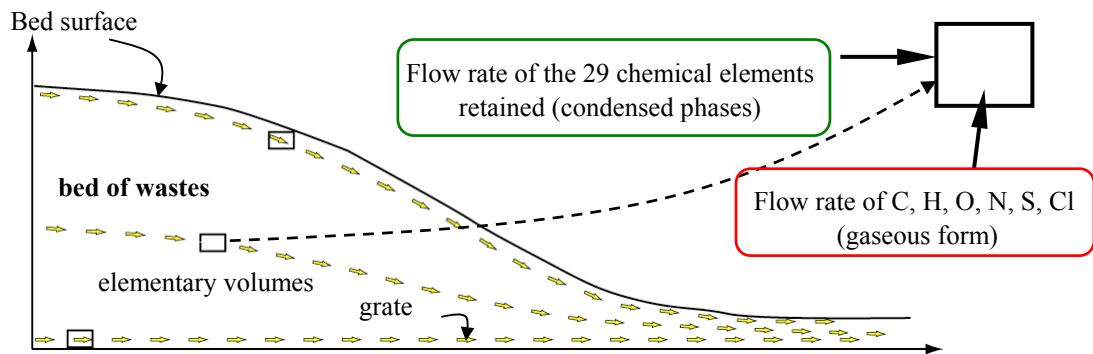


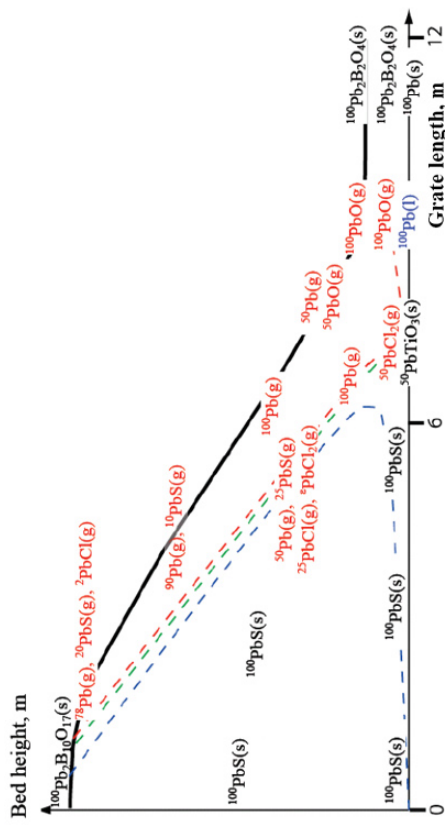
Figure 4. Principle of the local thermodynamic calculations in the refuse bed

Figure 5 synthesises the results of the thermodynamic calculations for the four metals considered. It presents, at selected locations, the different forms of these metals: chemical species, relative fractions, and phases. For cadmium, this figure shows that up to the drying front, the thermodynamically stable chemical form of cadmium is the sulphide CdS(s) and then the chloride $\text{CdCl}_2\text{(s)}$. Above the combustion front, stable cadmium is found in the vapour form 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 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 Cd(g) (over the whole height of the bed) implies that cadmium will indeed entirely vaporise and leave the bed as metal vapour Cd(g) and, in smaller quantity, as chloride $\text{CdCl}_2\text{(g)}$.

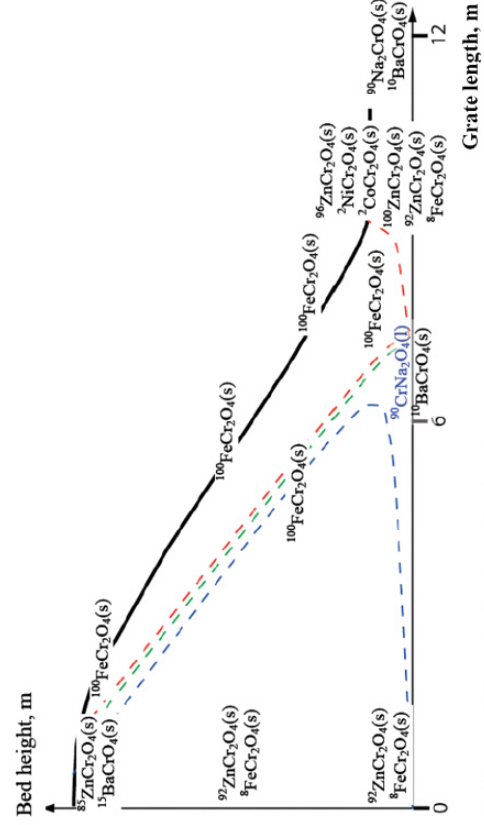
The chemistry of lead is more complex than that of cadmium. At the entrance of the grate, the stable form of lead is the solid sulphide PbS (melting point = 1386 K). Four chemical species appear above the combustion front in gas form: Pb(g) , PbS(g) , PbCl(g) and $\text{PbCl}_2\text{(g)}$. The chloride and sulphide forms then disappear to make space for the oxide PbO(g) . Again, the extent of the gas stable species zone suggests a high volatilisation of lead, though lower than that of cadmium. In the cold ash, stable lead is found as either the solid oxide $\text{Pb}_2\text{B}_2\text{O}_4$ or the simple metal Pb , in the liquid and then in the solid form (melting point = 600 K). The temperatures close to the grate are around 850 K downstream the oxidation front of the residual carbon (8 m from the grate entrance) and then diminish to less than 600 K towards the end of the grate.

Zinc, in the cold zone situated upstream the drying front, is mainly stable in the form of the mixed oxide $\text{ZnCr}_2\text{O}_4\text{(s)}$. Above the fronts, zinc can leave the bed in the vapour form Zn(g) or in the form of chloride $\text{ZnCl}_2\text{(g)}$. However, in the lower part of the bed, the vaporisation of zinc is small due to its stability in the form of solid oxides ZnFe_2O_4 and ZnCr_2O_4 . Behind the oxidation front of the residual carbon, zinc is stable in the form of several mixed solid oxides: ZnFe_2O_4 , ZnAl_2O_4 , ZnCr_2O_4 and Zn_2SiO_4 . The proportion of zinc in the bottom ash should thus be greater than that of cadmium and lead.

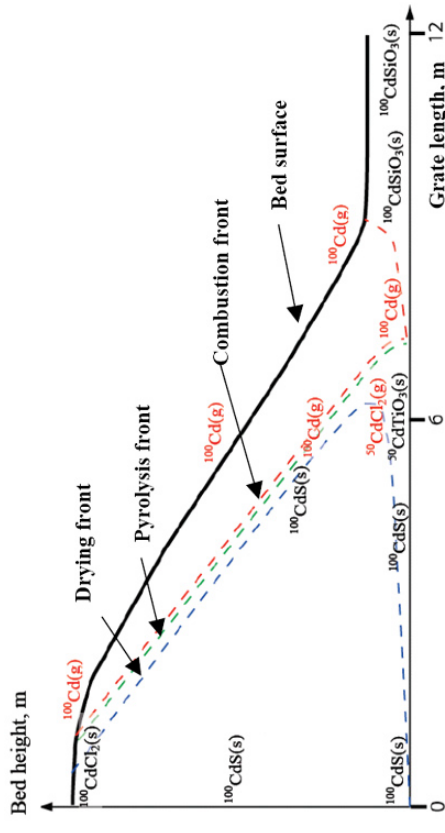
Lastly, Figure 5 proves the weak volatile character of chromium in the conditions of incineration of the MSW. Indeed, chromium is stable in the forms of various mixed solid oxides (iron, cobalt, zinc, barium and even sodium). No gaseous species is predicted for chromium.



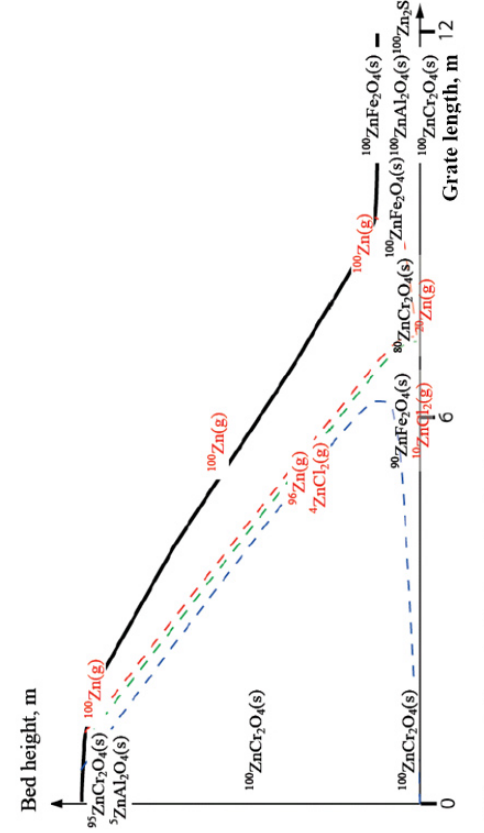
a) Pb speciation in the burning bed



b) Cr speciation in the burning bed



c) Cd speciation in the burning bed



d) Zn speciation in the burning bed

Figure 5. Heavy metal speciation in the burning bed. (s)=solid phase, (c)=condensed phase (solid or liquid), (g)=gaseous phase. The left exponent figures indicate the relative fractions at equilibrium.

3.2 Heavy metal speciation in the post-combustion chamber and the boiler

The simulations with FLUENT provide the local values of temperature and concentrations of the different gases, which are used for the thermodynamic calculations. As in the bed, the latter calculations are not performed for all points of the domain. Here, four streamlines were selected, from the bed surface at abscissas 0.5, 4, 8, and 11 m, to the boiler outlet.

In the current state of our FLUENT model, some species are not directly handled and their concentration 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 et al. (1995) and Brunner et al. (1986). For the four heavy metals considered, the concentrations in the gas are calculated assuming a given fraction vaporised 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 reactional 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 Cd(g) and then as chloride CdCl₂(g) over the hottest part of the combustion zone. Above the last few meters of the grate the oxide CdO(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 CdCl₂(g). Due to the cooling down of the gas in the heat exchanger, the solid sulphate CdSO₄ 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 CdCl₂ are as likely to be found in the ashes under the boiler or filters as CdSO₄.

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 meters 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 (1160 K). 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).

3.3 Comparison of the results of thermodynamic calculations to the experimental analysis

Concerning cadmium, the thermodynamic results for the burning MSW bed predict cadmium vaporisation in its elementary form or as chloride CdCl₂ in the whole hot zone of the bed. This indicates a significant volatilisation of this metal, in agreement with the experimental analyses (Brunner et al., 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 vaporisation. 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 vaporisation of lead whereas the experimental analyses show that 60 % of lead is localised in the bottom ash after combustion (Brunner et al., 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 vaporisation 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 ($ZnCr_2O_4$, $ZnFe_2O_4$, $ZnAl_2O_4$, Zn_2SiO_4). The volatility of zinc is thus lower than that of lead, as observed in experiments (Brunner et al., 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.

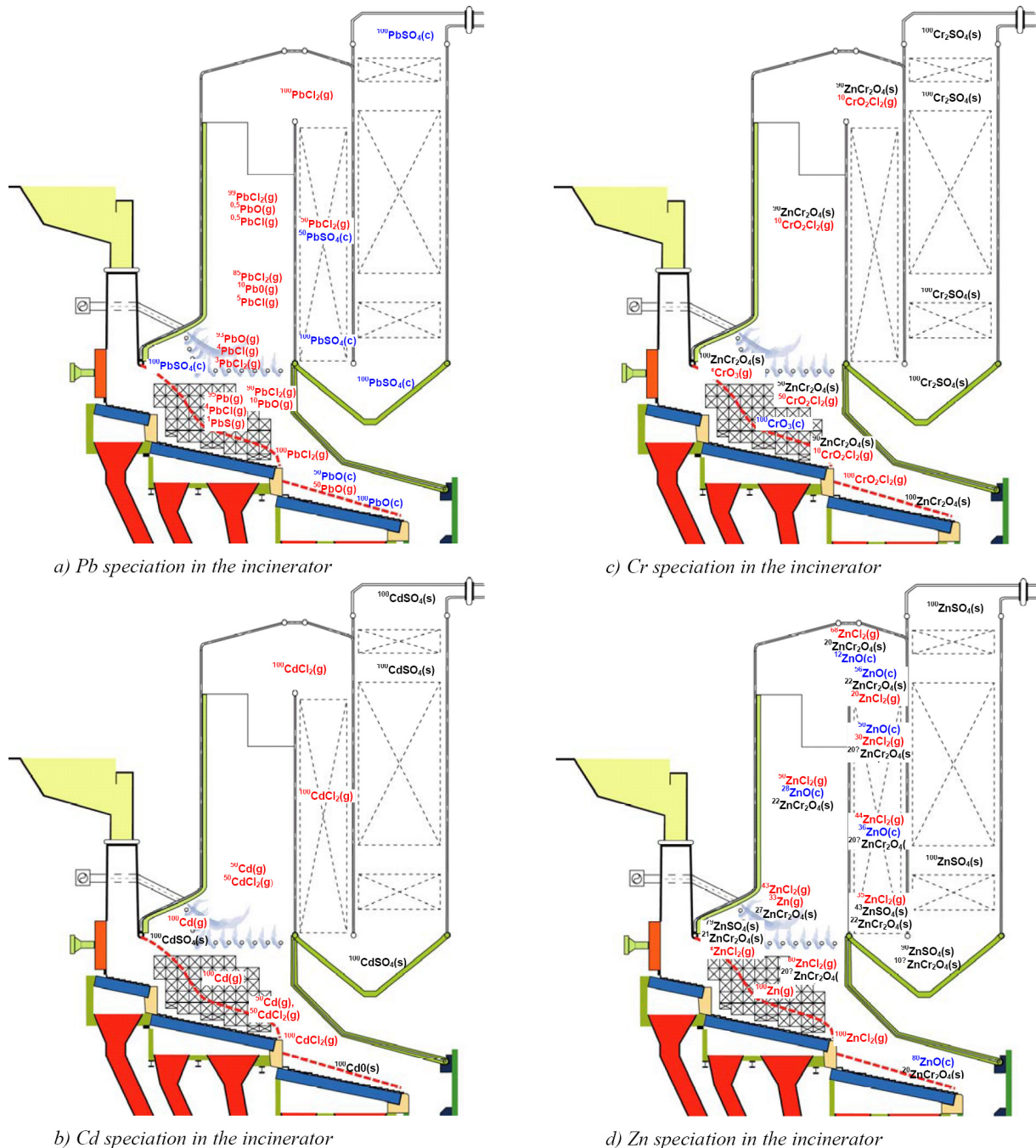


Figure 6. Heavy metal speciation in the incinerator. (s)=solid phase, (c)=condensed phase (solid or liquid), (g)=gaseous phase. The left exponent figures indicate the relative fractions at equilibrium.

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. PbCl_2 was identified by Gagnepain in the ashes under the boiler. Eighmy et al. identified PbSO_4 , PbCl_2 , PbO and Pb in electrostatic filter ash, in agreement with our thermodynamic results. According to Gagnepain, zinc appears as metal, in the form of oxides, of chlorides on the surface of dust, of sulphates, carbonates, aluminates, silicates, and as ZnCrO_4 in all the residues. Eighmy et al. identified ZnBr_2 , ZnCl_2 , 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 CrO_3 oxide, FeCrO_4 and ZnCrO_4 in the slag and MgCrO_4 (identified by Gagnepain) and PbCrO_4 (identified by Eighmy et al.) in the boiler ash. Thermodynamic calculations also reveal a stabilisation of chromium in many mixed oxides such as FeCr_2O_4 , ZnCr_2O_4 , NiCr_2O_4 , CoCr_2O_4 as well as the formation of $\text{Cr}_2\text{SO}_4(\text{s})$, $\text{Cr}_2\text{O}_3(\text{s})$, $\text{CrO}_2\text{Cl}_2(\text{g})$ and $\text{CrO}_3(\text{g})$.

4. 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.

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