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## HEAVY METAL VAPORIZATION IN FLUIDIZED BED COMBUSTION OF SOLID WASTE AND COAL

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### ABSTRACT

Solid samples, either of realistic waste model or coal, and spiked with Cd, Pb or Zn, were burned in an electrically-heated fluid bed reactor coupled to a customized ICP spectrometer, for on-line analysis of vaporized metals. For waste samples, a single kinetic law (whatever the metal), predicting the vaporization characteristic time and the time course of the metal concentration in the solid, was obtained. Tests with burning coal samples, spiked with Cd (at 820°C) and Zn (temperature range 680°C to 820°C), proved that this law is still valid, with a slight tendency to underestimation for both Cd and Zn vaporization rates. The transient metal concentration in burning coal was also very well predicted.

### INTRODUCTION

On the one hand fluidized bed technology is widely used for combustion processes dealing with coal and solid waste (municipal waste, dry sewage sludge). Recent studies have been dealing also with low grade fuel mixture processing, especially biomass mixture, in the presence of oxygen (co-combustion) or not (gasification).

On the other hand possible metallic emissions from coal combustors and waste incineration plants become a great environmental concern because of their toxicity for both human health and environment. So, endogenous heavy metals (HM), which may be emitted in the gases exiting the high temperature reactor (1, 2), impose a costly gas treatment unless the conditions inside the reactor are adapted to limit the metals' vaporization. Therefore, the release mechanism of metals during high-temperature waste treatment or coal combustion must be better known to improve the knowledge of their behavior, thus their emissions control. Incineration conditions (furnace temperature, chlorine, oxygen and moisture content, waste residence time...), in addition to the HM physico-chemical properties and to many other

parameters, strongly affect their behavior, then their partitioning (i.e. [3](#), [4](#)). Although many thermodynamic calculations ([5](#) to [8](#)) have been realized in order to discuss and predict the HM chemical speciation and fate, kinetic studies are the only way to predict the transient behavior of the system. Ho et al. ([9](#)) developed first a model and identified kinetic parameters with respect to experimental results. Later, our group determined kinetic rate laws for metal vaporization from incinerated waste ([10](#), [11](#)), applying an inverse method developed before ([12](#)) on experimental results obtained on a unique facility coupling a high temperature fluid bed reactor to an ICP spectrometer for measuring online the metal concentration in the outlet gas. In the temperature range 650°C-800°C, the vaporization rate is expressed as a function of the metal concentration in waste, for any studied metal (Cd, Pb, Zn).

In this paper, two main types of metal-spiked fuel were burned in the combustion-incineration simulator: a solid realistic waste model, which simulates municipal solid waste and sewage sludge as well, and coal. The same three representative metals (Cd, Pb, Zn) were considered. Their behavior was first compared depending on the type of fuel. Secondly, the law was experimentally validated by a series of experiments run with other metal-spiked waste samples. Then, in order to see how general this law can be, although drawn from experiments dealing with solid model waste only, it was tested on burning coal samples, spiked with Cd (at 820°C) and Zn (temperature between 680°C and 820°C).

## EXPERIMENTAL STUDY

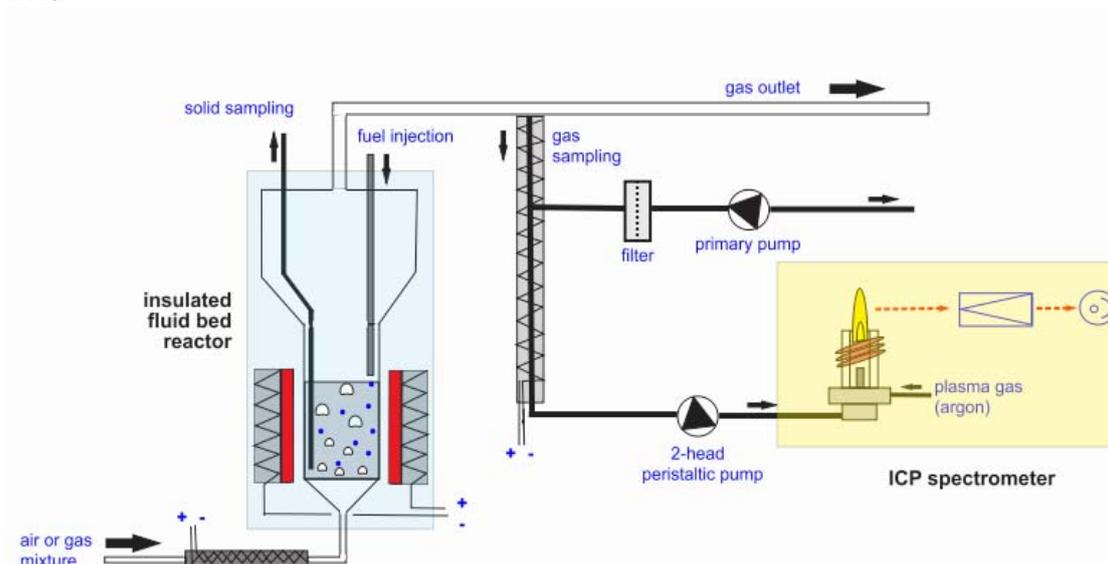
### Experimental setup

The experimental setup is composed of a high temperature, electrically-heated, fluidized bed reactor, 0.105 m ID, coupled to a customized ICP spectrometer (Fig. 1). The 0.7 mm diameter sand bed is fluidized by a preheated gas (air or mixture) and maintained at the desired temperature by 2 half-cylinder radiative shells. K-thermocouples measure the temperature at several depths in the bed, as well as at the gas inlet and outlet. When at steady state, a given mass of reactive metal-spiked waste particles is injected into the bed, thanks to a compressed air device. Then, the HM is vaporized and emitted in the outlet gas. A heated 6m-long sampling line connects a spectrometer to the reactor gas outlet for metal analysis. The metal concentration is measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The spectrometer (Horiba Jobin Yvon 38S) was customized in order to allow gas injection into the argon plasma, since originally it was designed for elemental analysis in liquids. Finally, the vaporized metal concentration in the gas can be measured online by implementing a calibration procedure developed before ([13](#)).

### Experimental procedure

First set of experiments was carried out with a realistic artificial waste (RAW), consisting in a mixture of flakes of real solid waste, sand (wt. ratio 2-to-1), glue and metallic salt, pressed into cylinders (dia. 1cm, H 1 cm) and dried at 80°C. This artificial waste, whose ash content is about 20 wt.%, simulates very well both municipal solid waste and sewage sludge. As shown in Table 1, the resulting metal content of RAW, ranging from 700 to 1000 mg/kg, was within the same range as

encountered in real waste for Pb and Zn, about one hundred-fold for Cd (1). A high enough metal concentration in substrate is required because of the ICP detection limit.



**Figure 1:** Experimental setup

The second part of the experimental study was carried out with coal particles. Particles (mean diameter 8 mm, ash content 27%) were spiked with Cd and Zn by impregnation in a liquid solution of metallic salt: a weighted batch of substrate was mixed for 5 h with the appropriate volume of metallic species solution, then samples were dried at 80°C for at least 24 h. The resulting metal concentration in coal samples is displayed in Table 1 (14); it is 100 to 1000 times the concentration range encountered in natural coalfields. Again, this metal excess in samples is necessary in order to get significant metal emissions, thus significant metallic concentrations for gas analysis.

Table1: Metal concentrations in samples, in waste and in coal

	Concentration (mg/kg)		
	Cd	Pb	Zn
RAW samples	700-1000	700-1000	700-1000
Typical municipal waste (1)	5-15	400-1000	500-2000
Spiked coal samples	1065	-	2660
Typical coal (14)	0.1-10	-	10-100

The procedure was as follows, combining both experimental and theoretical approaches:

- Measurement of the initial metal concentration in the solid sample by classical ICP spectrometry after acid digestion of particles.
- Injection of a given amount of metal-spiked particles (RAW or coal) into the bed (at thermal steady state).

- Online measurement of the time course of the metal concentration in the exhaust gas by the customized ICP-OES technique.
- Calculation by inverse method of the metal vaporization rate at the particle level.
- Identification of a kinetic rate law from the vaporization rates found at various temperatures.

## GENERAL KINETIC RATE LAW FOR METAL VAPORIZATION FROM WASTE

First series of experiments was carried out with realistic artificial waste, spiked with Cd, Pb and Zn, at several temperatures: 650°C, 680 °C, 710 °C, 740 °C, 770 °C, and 800 °C.

Implementing the procedure described in previous section, the online HM concentration measurement leads to the HM vaporization fluxes, that-is-to-say to plots of the metal vaporization rate ( $r = -dq/dt$ ) versus the metal concentration in waste ( $q$ ). Then, for each metal, a specific rate law, which depends on temperature, may be drawn (11):  $r = -dq/dt = k(T)q^n$ .

The next step consists in generalizing all these laws into a single dimensionless mathematic law expressing the solid matrix influence on the metal vaporization dynamics, whatever the metal and whatever the temperature in the considered range. It is obtained as follows:

- 1/ change the variables  $x = (q_0 - q)/(q_0 - q_f)$  and  $r_{ad} = r/r_{max}$
- 2/ plot  $r_{ad}$  versus  $x$  for all data, that-is-to-say 3 metals in artificial waste, 6 temperatures;
- 3/ fit all points to a  $n^{th}$ -order polynomial  $f(x)$ , expressed differently for the increasing section and for the decreasing section;
- 4/ identify the global kinetic rate law to the polynomial  $f(x)$ .

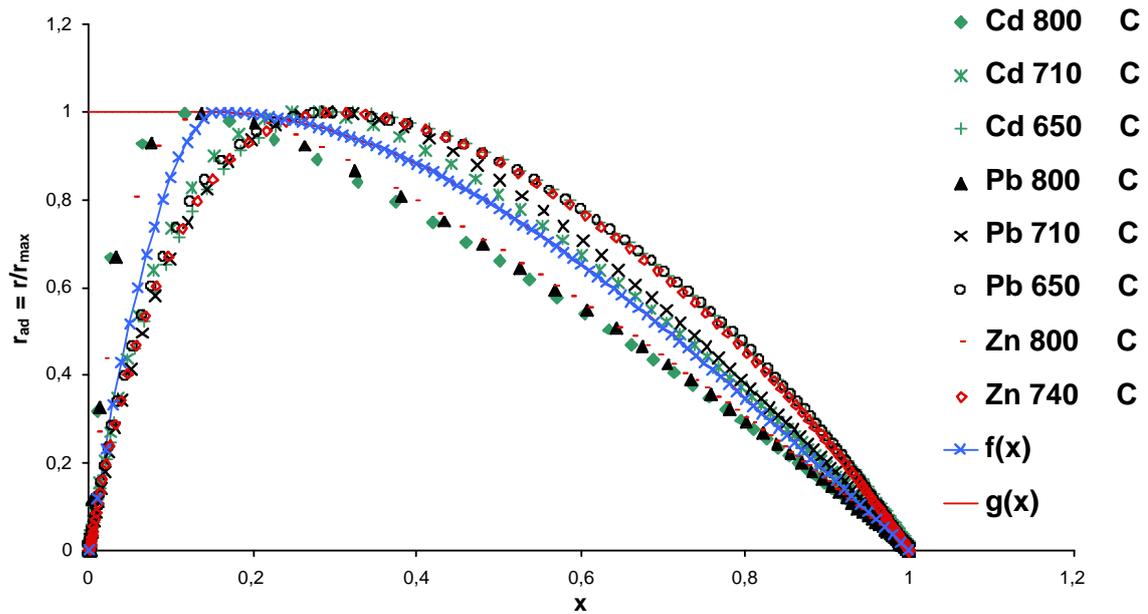
The general mathematical expression  $f(x)$  obtained by this procedure is:

$$(1) \begin{cases} 0 < x < x_m & f(x) = -5/6 (x/x_m)^2 + 11/6 (x/x_m) \\ x_m < x < 1 & f(x) = 1/2 [(x - x_m)/(1 - x_m)]^3 - 3/2 [(x - x_m)/(1 - x_m)]^2 + 1 \\ x_m = 0.15 & \end{cases}$$

Actually,  $x_m$  represents the HM concentration in the waste from which the vaporization rate (i.e. the instantaneous slope of the transient metal concentration) starts decreasing. It was shown before that the first part of the vaporization process (when  $r_{ad}$  increases from 0 to 1) is negligible since less than 5 wt% of the metal is vaporized (15), whatever the metal. Therefore, we may assume the vaporization rate is constant and maximal at the beginning of the vaporization process. This leads to the following global law  $g(x) = - (dq/dt)/r_{max}$ :

$$(2) \begin{cases} 0 < x < x_m & g(x) = 1 \\ x_m < x < 1 & g(x) = 1/2 [(x - x_m)/(1 - x_m)]^3 - 3/2 [(x - x_m)/(1 - x_m)]^2 + 1 \\ x_m = 0.15 & \end{cases}$$

Figure 2 plots the whole set of experimental results and both laws  $f(x)$  and  $g(x)$ . The general law  $g(x)$  was validated by independent experiments, ran with RAW particles spiked with other concentrations of Cd, Pb and Zn. For all three metals, at 650°C as well as at 800°C, metallic vaporization rates were very well predicted by the general law (15), thus indicating this law can be used satisfactorily in this temperature range to predict any metal vaporization kinetics from burning waste particles. The vaporization characteristic time and the time course of the metal concentration in the waste can be predicted with a good accuracy whatever the metal.

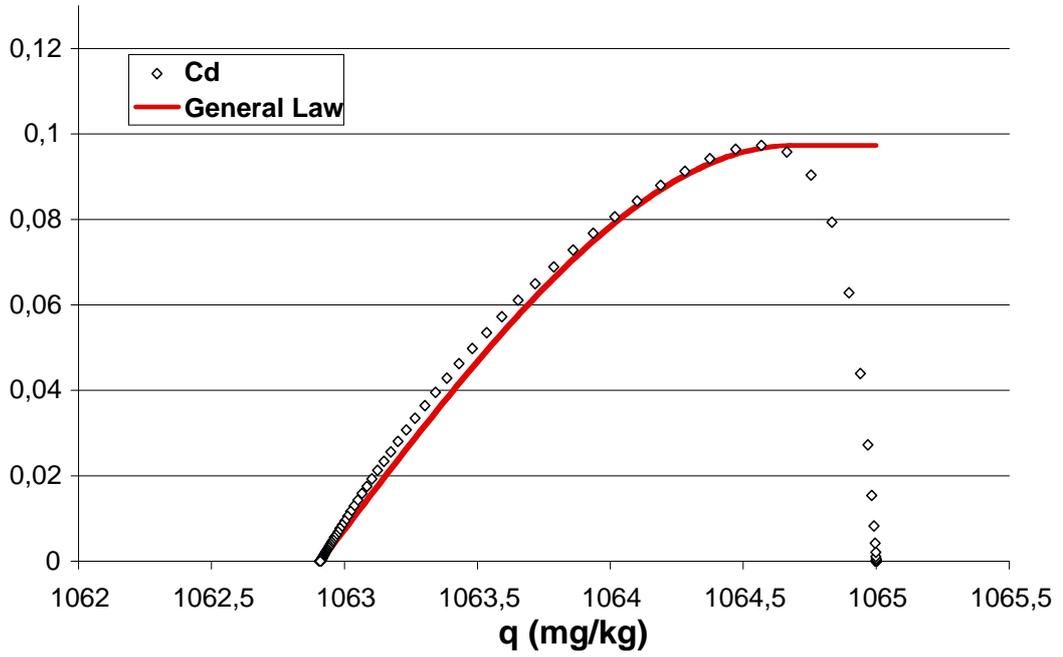


**Figure 2:** Normalized kinetic rates and general kinetic rate law (waste incineration)

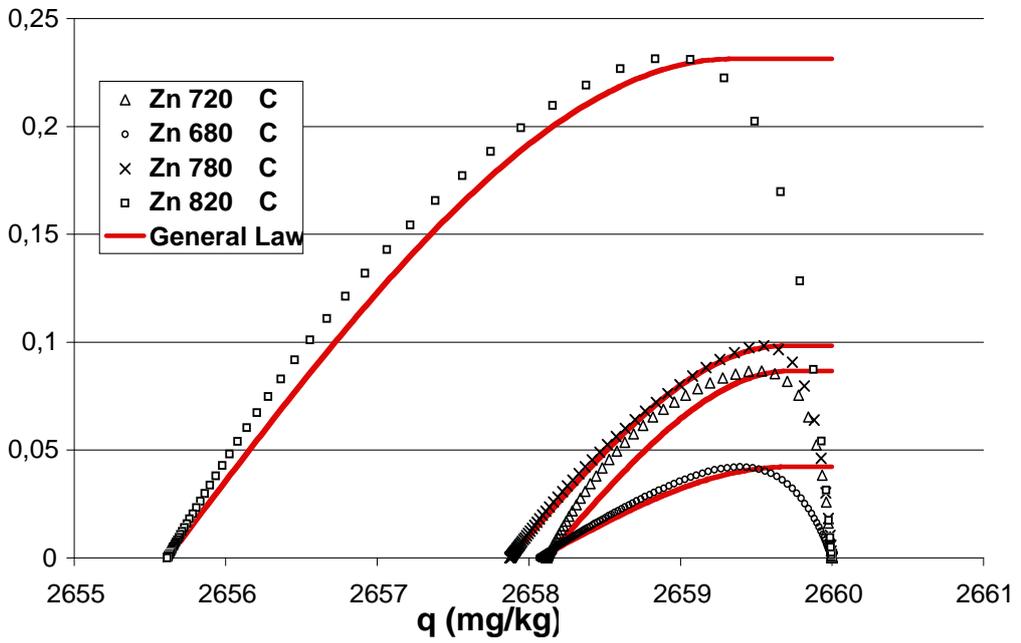
## CASE OF METAL VAPORIZATION FROM COAL

### Validity of the general kinetic rate law

In order to see how general this law can be, although drawn from experiments dealing with solid model waste only, it was used to predict the behavior of burning coal samples, and theoretical prediction were confronted to experimental results. Experiments were carried out with the same experimental setup involving the fluidized bed coupled to the ICP spectrometer. Coal particles, spiked with either Cd (at 820°C) or Zn (various temperatures ranging between 680°C and 820°C) were injected in the bed at steady state. As shown on Figures 3 and 4, both Cd and Zn vaporization rates were very well predicted by the law, although with a slight tendency to underestimation. The coal thermal conductivity is higher than that of the waste, which may explain why the law (drawn from experiments ran with waste only) underestimates the metal's vaporization rate when dealing with coal: the thermal front moves faster in coal, so does the vaporization front, and therefore the vaporization rate is higher in coal than in waste.



**Figure 3:** Cd vaporization rate from coal combustion ( $T = 820^{\circ}\text{C}$ )



**Figure 4:** Zn vaporization rate from coal combustion ( $T = 680^{\circ}\text{C}, 720^{\circ}\text{C}, 820^{\circ}\text{C}$ )

**Prediction of the metal concentration evolution in coal**

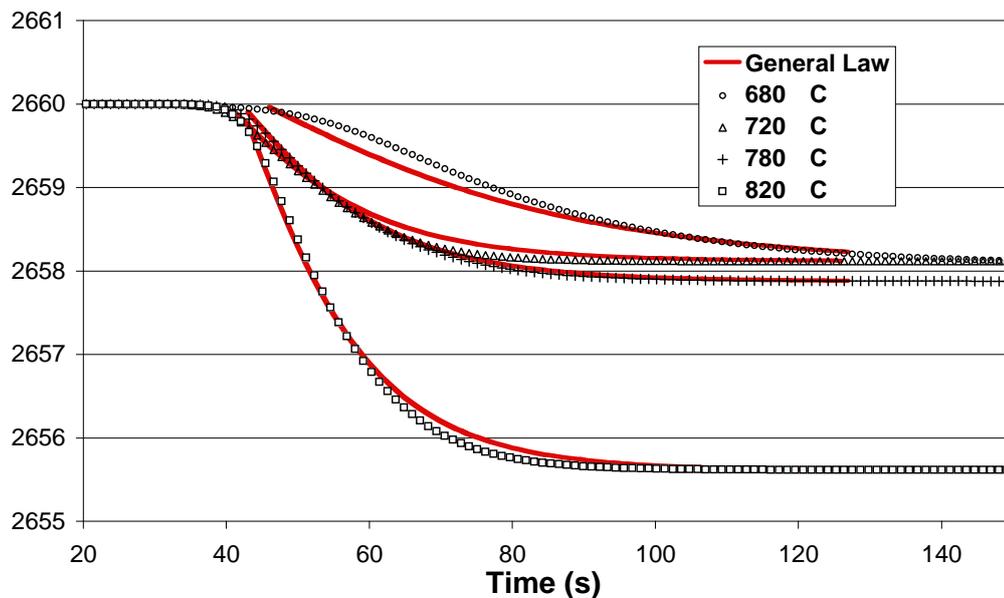
The metal concentration in the substrate  $q(t)$  can be determined by solving the differential equation (2), thanks to the change of variables

$$X = (x - x_m)/(1 - x_m) \quad \text{and} \quad t^* = t \cdot r_{\max} / [2(q_0 - q_f)]$$

Finally, the metal concentration time course is:

$$q = q_0 - (q_0 - q_f) \left[ 1 - \sqrt{\frac{3/2}{e^{3r_{\max}t/(q_0 - q_f)} + 0.5}} \right]$$

Figure 5 plots the general law prediction of the transient metal concentration in coal, and compares the prediction to experimental results. The prediction is always very good, although at lower temperature the metal release is slightly overestimated. Moreover, Cd release from burning coal at 820°C was very well predicted.



**Figure 5:** Zn concentration time course in burning coal

**CONCLUSION**

A general kinetic law describing the heavy metal vaporization from burning waste particles was obtained. It predicts the vaporization rate and the time course of the metal concentration in the solid. Coal samples, spiked with Cd and Zn, were burnt: these tests showed this law can be extended satisfactorily to the case of coal combustion although drawn from experiments dealing with waste combustion. Indeed, both the metal vaporization rate and the transient metal concentration in burning coal are very well predicted by the general law.

## ACKNOWLEDGEMENT

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