

# The partitioning of heavy metals in incineration of sludges and waste in a bubbling fluidized bed

## 2. Interpretation of results with a conceptual model

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### Abstract

This work addresses the behavior, fate and/or partitioning of six targeted (Cd, Pb, Cr, Cu, Zn and Ni) heavy metals (HMs) in the incineration of sludges and waste in a bubbling fluidized bed (BFB) of 15 cm i.d. and 5.2 m high followed by a filter chamber operated at 750–760 °C with a commercial ceramic filter. This paper presents three different things: (1) an in depth review of the published work relating to the problem of partitioning of the HMs in BFBs, (2) some more experimental incineration tests regarding the influence of the temperature of the bed of the BFB and the effect of the chlorine content in the feedstock on the partitioning of the HMs, and (3) the modelling of the partitioning of the HMs in the exit flows: bottom ash, coarse fly ashes, fine fly ash and vapour phase. The partitioning of the HMs is governed by fluid dynamic principles together with the kinetics of the diffusion of the HMs inside the ash particles and the kinetics of the reactions between the HMs and the components of the matrix of the ash. Some thermodynamic predictions do not fit the results from the BFB incinerator well enough because equilibria are not reached in at least three exit ash flows: coarse fly ash, fine fly ash and submicron particles. The residence time of these ash particles in these type of incinerators is very short and most of the HMs have no time to diffuse out of the ash particle. Finally, an examination was made on how in the ceramic hot filter the partition coefficients for the HMs increased, mainly for Cd and Pb, when the Cl-content in the feedstock was increased.

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### 1. Introduction

Incineration or combustion of different types of sludges, residues and waste in fluidized bed (FB) is a technology, which has reached a commercial level of operation (EBARA, Foster Wheeler and KVAERNER processes, for example). It has well known advantages and problems; one of these problems being the emission of some pollutants. Among these pollutants, this paper is only concerned with the behaviour and emissions of heavy metals. Although these heavy metals have been called trace elements, trace metals, toxic metals,

... here they will be simply called heavy metals (HMs). Even though some other heavy metals such as Hg, Mo, V, Mn, As, Sb, Se, ... are also of the greatest concern (e.g. Hg) or moderate concern (e.g. V), the experimental work and modelling presented here was done with only six targeted HMs: Cd, Pb, Cu, Cr, Zn, Ni. Due to the importance of the emissions of HMs from incinerators, a lot of work has already been made in the last 15 years and even complete books [1,2] have been written about this problem. Nowadays, this issue is very well known so no basic questions will be addressed in this paper. The aim of this paper is, therefore, to present some conclusive facts and to understand the partitioning of HMs during incineration in bubbling fluidized beds (BFBs).

The study and modelling presented in this paper are based on two different sources: our own research at a small pilot plant scale and on an extensive review of the published work

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Table 1  
Authors who have studied the partitioning of the HMs in incineration or combustion in fluidized bed

Authors	Country	Waste used	Bed material/solid sorbent	Incinerator type	Ref.
Corella and Toledo	Spain	Industrial and sewage sludges	Silica sand	BFB	[3]
Lighty et al.	USA	Industrial and simulated sludges	–	Rotary kiln and CFB	[4–9]
Koziński et al.	Canada	Biosludges	Silica sand	BFB and CFB	[6–10]
Mininni et al.	Italy	Sewage sludges	Sand	CFB	[11–13]
Lee et al.	Korea	Sewage and dye sludge	Sludge-derived ash	Swirl-flow BFB	[14–16]
Barton et al.	USA	Sewage sludge		Multiple heart and BFB	[17,18]
Ho et al.	USA	Simulated waste	Sand, limestone, alumina,	BFB	[19–21]
Wey et al.	Taiwan	Waste	Different sorbents	BFB	[22–26]
Chang et al.	Taiwan			Fixed bed	[27]
Wang and Lin	Taiwan		Bentonite, alumina, . . .	BFB	[28]
Coda, Berger et al.	Germany, Sweden and Finland	Blends of coal, straw and paper sludge, sewage sludge	Silica sand, additives, limestone	BFB	[29–31]
Lundberg et al.	Sweden	MSW, RDF wood-waste		BFB	[32]
Bridle and Rovel	Australia and France	Sewage sludge (pyrolysis)		“Converters A and B”	[33]
Reed, Kandiyoti et al.	UK	Coal, blends of coal with biomass, sludges, wastes, sludge gasification		FB “suspension firing”	[34–38]
Flamant et al.	France	MSW	Sand, alumina, sepiollite	BFB	[39–42]
Kouvo et al.	Finland	Wood, peat, RDF blends	Sand and limestone	BFB	[43,44]
Latva-Somppi, Kauppinen et al.	Finland	Sludges	Quartz sand and ashes from the sludges	BFB and CFB	[45,46]
Lind, Kauppinen et al.	Finland	Coal, biomass	Limestone and ash	CFB	[47–49]
Aho et al.	Finland	Biomass, sludge, plastic waste	Natural sand	BFB	[31,50,51]
Guyurthu et al.	Portugal	Mixtures of coal and residues		BFB	[52,53]
Åmand and Leckner	Sweden	Mixtures of sludge, coal and wood	Limestone	CFB	[54]
Jung et al.	Japan	MSW	Not said	7 FBs	[55]
Bajohr et al.	Germany	Biomass	None	Entrained flow gasifier	[56]
Lu et al.	P.R. China	Coal	None	BFB	[57]
Linak and Wendt	USA	Extensive review paper			[58]
Ruth	USA	MSW	Bauxite	BFB	[59]
Salo and Mojtahedi	Finland	Biomass	Not said	FBG	[60]

made worldwide. There is a huge amount of literature and data published on the distribution, behaviour and/or partitioning of the HMs during incineration in fluidized bed, and this is summarized in Table 1. Although a quantitative synthesis of the similarities and differences between the important publications shown in Table 1 was not made because of the huge amount of data contained in them, most of these publications arrive to similar conclusions on the partitioning of HMs in incineration or combustion in fluidized bed.

In Table 1 are included some papers on sludge/waste incineration in fluidized bed with a few additional papers on the fate of HMs in BFB coal pyrolyzers and combustors, and in biomass and sludge pyrolyzers and gasifiers [33,34,38,56,57,59]. The reason for including these papers is because the results on partitioning of the HMs in these

processes agree with those found in sludge/waste incineration in FBs. It is therefore believed that the main conclusions arrived in this paper might also be applied to BFB pyrolyzers, gasifiers and combustors of coal, biomass and different types of sludge.

Most of the former incineration tests made at UCM [3] were carried out under the EC-financed MELODI project aimed at studying the fate or partitioning of HMs in waste/sludge incineration. In the MELODI project, several other types of incinerators were used such as two rotary kilns from INDAVER s.a. (Antwerpen, Belgium) and FZK (Karlsruhe, Germany), one grate-type (TAMARA facility) at FZK and one fixed bed from INETI (Lisbon, Portugal). The partitioning of HMs in all these different types of incinerators was different. A partner in that project, THERMODATA

(Grenoble, France), used his GEMINI software, based on thermodynamic principles, to predict the behaviour and fate of the heavy metals in the incinerators. The thermodynamic calculations were good enough to predict the behaviour of the HMs in grate-type incinerators [61], for example, but did not fit well with the partitioning of HMs obtained in the BFB at the University Complutense of Madrid [62]. These results from thermodynamic-based models were not good enough for predictive purposes in fluidized bed incinerators, as was already reported by other researchers (e.g. [18,35,38,55,58]). Even some authors that use thermodynamic equilibrium modelling approaches clearly recognize important limitations of these models [37].

It is therefore clear that there are important discrepancies in the partitioning of HMs between the different types of incinerators and also that some thermodynamic calculations to predict the fate of some HMs may generate results different from those obtained in BFB incinerators where some kinetic aspects may control the fate of the HMs. Therefore this paper aims to make a deeper study of the fate of HMs in BFBs and to develop a conceptual model to explain and fit the results of the behavior and partitioning or fate of the HMs in BFB incinerators. Besides our already published data [3], some more incineration tests were made at UCM to validate some concepts.

## 2. Experimental facility and feedstock used

The BFB incinerator used for this paper was described previously [3] and it is shown in Fig. 1 which corresponds to its latest configuration. It has an internal diameter of 15 cm and a total height of 5.2 m. It is fed directly in the bed, near the gas distributor plate, with flow rates of 1.2–2.5 kg/h corresponding to throughputs between 440 and 580 kg/h m<sup>2</sup> of cross-sectional area, not far from the values found in commercial BFB incinerators. The superficial gas velocity at the bed inlet was between 1.2 and 2.0 m/s, corresponding to an excess air (above the stoichiometric) of about 50% vol. The stable bed was silica sand together with some (bottom) ash from the feedstock. A part of the solid in the bed was periodically withdrawn by an exit pipe as shown in Fig. 1 to avoid increasing the amount or height of solid in the bed. Details on axial profiles of temperature and on air partitioning in the incinerator were given in [3].

The basic feedstock used for the experiment was a pre-dried sewage sludge from a waste water treatment plant in the city of Madrid. A detailed characterization of this sludge was previously given [3]. This feedstock did not have a content of some HMs high enough, and the sampling and chemical analysis could therefore have important errors for these HMs. For this reason, prior to its drying, the wet sludge, a slurry, was doped or spiked with salts of the six HMs to get contents between 4000 and 8000 ppms for each HM. The spiking of the wet (slurry) sludge was carefully made to further generate a homogeneous distribution of the HMs

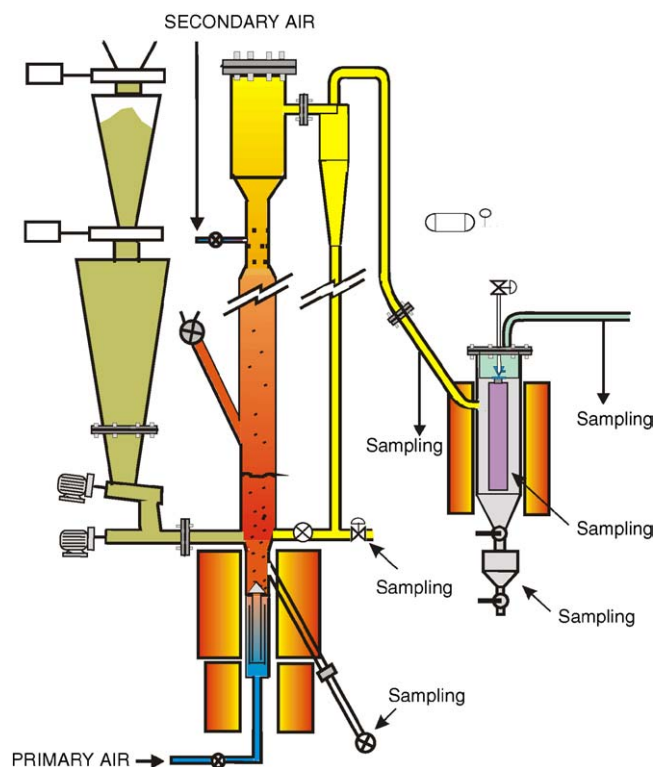


Fig. 1. BFB used at UCM for incineration of waste and sludges.

inside the particles of the sludge. Once the sludge dried, it was crushed and sieved. The details about the chemical composition and physical properties of the spiked sludge and its ash were also given before [3]. The salts used for doping or spiking were acetates, carbonates and nitrates of the HMs because when calcining they only generate CO<sub>2</sub> and NO<sub>x</sub> which do not remain in the sludge and can not therefore react with the matrix components. Probably the type of salt or species used in the spiking could have an effect on the behavior of the HMs during combustion because the binding force between the HMs and the matrix components has an influence on the time for their diffusing out of the matrix of the sludge. It may be accepted therefore that other salts of HMs might generate a slightly different partitioning of the HMs during the incineration process. Nevertheless, the main causes of this partitioning would remain the same.

After the BFB incinerator itself there was a cyclone and a filtering chamber. It was externally heated, operated at 750–760 °C and had a ceramic candle filter called PANTEL® from DIDIER Filtertechnik GmbH. Face velocities used in the filter were between 2 and 5 cm/s.

Each incineration test at UCM required about 2 person-months for cleaning, preparing and running the incineration facility, 2 person-months for chemical analysis and 1/2 person-month for managing, analysis of results, reporting, and so on. Therefore, 1 incineration test in this facility needed on average 4½ person-months.

Mass balances on the sludge and on each HM were made in all tests. Details of these mass balances and of feedstock preparation were given before [3].

### 3. Sampling and analysis of the ash for HMs

#### 3.1. Sampling

Sampling of solids (ashes) and gas (flue exit gas) for heavy metal measurements was made at the points indicated in Fig. 1. Apart from the feedstock, samples of solids were taken at:

- (1) the incinerator bed (bottom ash),
- (2) coarse fly ash, at the bottom of the cyclone,
- (3) fine fly ash (cake on the filter surface), collected at the bottom of the filtering chamber and at the end of the test,
- (4) flue exit gas (after the hot filter).

Sampling and analyses were made under steady-state conditions in the incinerator. These steady-state conditions were reached after a start-up period of around 3 h. Besides, the many years of operating this plant made it easy to know when the steady-state was reached. This steady-state operation was assured because all parameters such as temperature, pressures and flow rates were constant during this time.

In every incineration test-run, several samples of ashes were taken each hour from the different points or locations indicated in Fig. 1. Duplicate and triplicate analysis were then made from the same sample at the UCM's Center of Atomic Spectroscopy. The periodic samplings and the repeated analysis enabled an error evaluation to be made of the HM-content, which are now presented in this paper. These evaluations were made according to well known standardized statistical methods [63,64]. The calculated interval of error for the tests shown in this paper was in the 10–20% range. It is worth mentioning that the tests carried out during the first two years of this research are not included in this paper because they had errors larger than 20%. Furthermore, the error intervals are not included in Figs. 3–5 to make them easier to read.

#### 3.2. Analysis

Sampling and analysis were made using standard methods (such as the EPA method 23) but some latest developments in the analysis of HMs like those of Oikari et al. [51] were also taken into account. The samples of ash once dissolved were analysed for six metals (Cr, Ni, Zn, Pb, Cu and Cd) by ICP-AES (inductively coupled plasma–atomic emission spectrometry) at the UCM's 'Center of Atomic Spectrometry (CEA)'. The most advanced and standardised techniques were used. For instance, the sample of solid (ash) was first attacked (digested) with acid solutions (of FH, ClO<sub>4</sub>H, ...) following the procedure described in DIN 38414/7. Then, the solid residue was melted with lithium tetraborate at 950 °C using microwave digestion.

Some particles of ash were also analysed by a JEOL JXA 8900M electron probe microanalyzer (EPMA) equipped with five wavelength-dispersive spectrometers (WDS) at the UCM's "Center of Electron Microscopy". These analyses provided the cross-sectional distributions of the HMs in the ash particles, which were similar to those already found and published by the University of Utah [7–9].

### 4. The fate or partitioning of the HMs in the outlet flows

HMs have the following four different outlet flows in this facility (Fig. 1):

- bottom ash, in-bed material;
- coarse fly ash, at the bottom of the cyclone;
- fine fly ash (as a cake on the filter surface). It is collected from the bottom of the filter chamber and from the filter surface at the end of the test;
- in the flue gas after the hot filter, as vapour or submicron particles.

These four outlet flows are schemed in Fig. 2. They are similar to those found in the work of Åmand and Leckner [54], excepting that they used a bag filter instead of a high

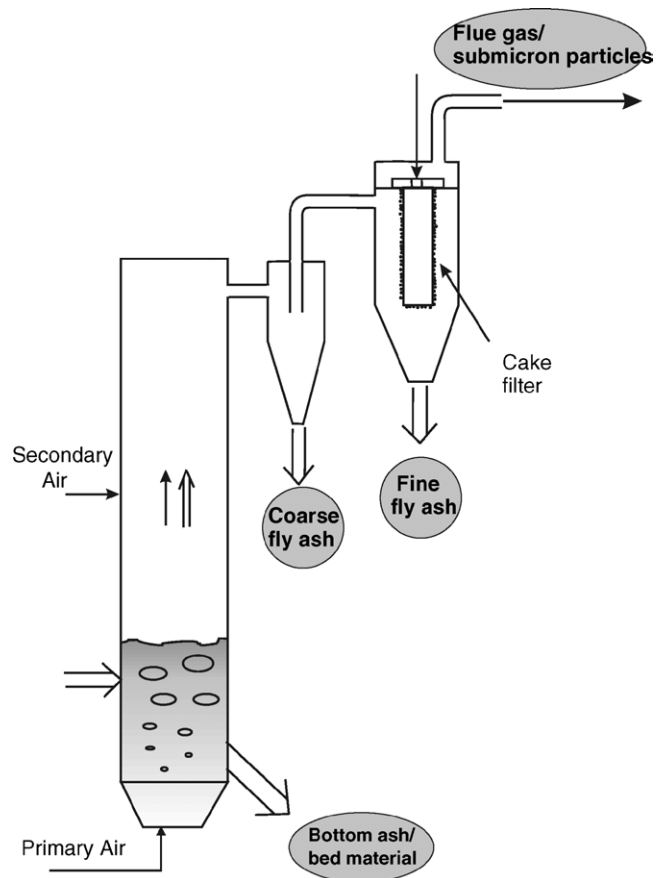


Fig. 2. Exit flows for the HMs in the BFB based incineration plant.

temperature ceramic filter as was the case of the present work.

After the chemical analysis of each sample and with the indicated mass balances, the fate, distribution or partitioning of each heavy metal was calculated. Most of these partitionings were shown previously [3], but a few more recent results are presented here.

#### 4.1. Effect of the temperature of the incinerator bed

Experimental data are shown as the percentage of the targeted HM in a given exit flow. This percentage is precisely defined as:

$$P_i = \frac{\text{mass (g) of the } i\text{th HM in a given exit flow}}{\text{total mass (g) of the } i\text{th HM in the four or total exit flows}} \times 100 \quad (1)$$

Under steady-state conditions the total mass of a HM in the four or total exit flows is equivalent to the input mass of the HM to the incinerator. These ratios are therefore equivalent to the partition coefficients ( $k_i$ ) used by Lee and co-workers [14–16], who calculated and reported only two partition coefficients (bottom bed and fly ash collected by cyclones).

Only the two extreme (Cd and Ni) cases of behaviour among the six HMs studied here will be shown in detail. Error bars in all points are omitted for better understanding of the figures.

**Cadmium:** The other conditions being the same, an increase of temperature (between 855 and 905 °C) in the bed ( $T_b$ ) of the BFB incinerator has the following effects on the Cd content:

- The Cd content increases in the flue exit gas, as vapour phase and/or submicron particles, as shown in Fig. 3.
- The Cd content decrease slightly in the bottom ash with  $T_b$ . Due to the high volatility of cadmium, part of it is lost from the ash particles that remain a relatively long time in the bed, i.e. the bottom ash.

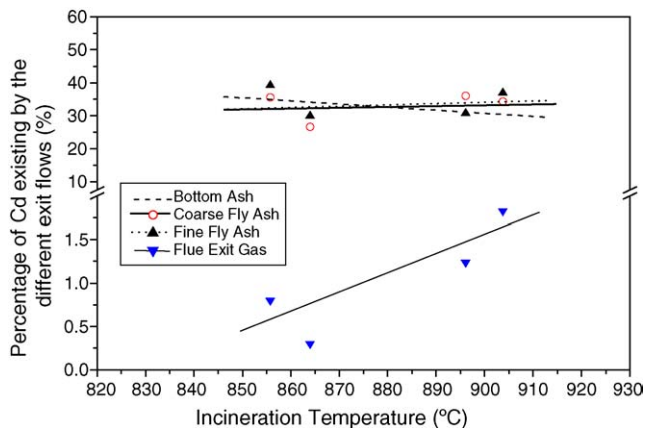


Fig. 3. Effect of the temperature of bed of the BFB incinerator, on the distribution of the cadmium, for a given superficial gas velocity at the inlet (1.3–1.5 m/s) and particle size (<4 mm) of the feedstock.

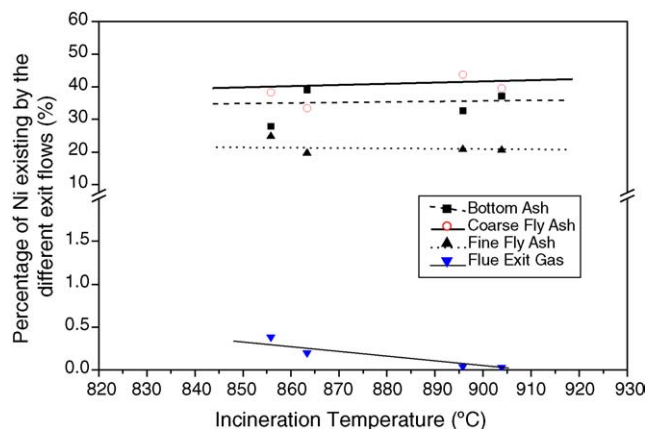


Fig. 4. Effect of the temperature of the bed of the BFB incinerator, on the distribution of the nickel, for a given superficial gas velocity at the inlet (1.3–1.5 m/s) and particle size (<4 mm) of the feedstock.

- The Cd content does not vary appreciably with  $T_b$  in the coarse and in the fine fly ash because their residence time in the incinerator is very low.

**Nickel:** The nickel partitioning is shown in Fig. 4. Its amount or percentage in the flue outlet gas differs from that of cadmium in this outlet flow. Due to its low volatility, nickel is not transferred to the vapour phase. Instead, with an increase of  $T_b$ , nickel starts to be trapped or reacts with the mineral constituents of the ash (64 wt.%  $\text{SiO}_2$  and 30 wt.%  $\text{CaO}$ ) [3] and is retained in the particle.

Cr, Cu, Zn have a partitioning similar to that of Ni whereas Pb has an intermediate behaviour due to its intermediate volatility.

Even though comparison of results in this process is difficult because each author usually has his own way, form and/or manner of presenting his results, it can be said that all these results agree with most of the results published in literature to this concern.

#### 4.2. Effect of the Cl-content in the feedstock

The spiked sludge had a low content of chlorine, only 0.03 wt.%. To study the effect of the Cl-content in the feedstock, the sludge was mixed by hand with small chips of PVC in prefixed amounts to reach 3.0 wt.% of chlorine in the final feedstock. Incineration tests were carried out, the other conditions remaining the same, with feedstocks with and without PVC added. That-is-to say, the two feedstocks used had 0.03 and 3.0 wt.% of chlorine, equivalent to experimental [at.-g Cl/at.-g total metals] ratios of 0.003–0.010 to 3.6–3.9, respectively [3]. The theoretical or stoichiometric value for this ratio, for the chlorination reactions considered, is 1.9–2.0. It means that the Cl-content in the feedstock varied from sub-stoichiometric to over-stoichiometric for the chlorination reactions targeted, respectively.

The partitioning of the HMs among the bottom ash and the fine fly ashes was practically the same in these tests. Only

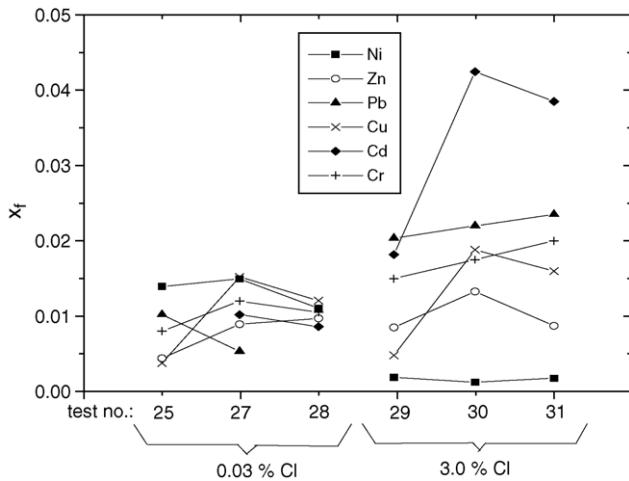


Fig. 5. Heavy metal partition coefficients in the hot ceramic filter (PANTEL® operated at 750–760 °C).

the partitioning in the hot filter was different. To describe the behaviour of the HMs in the hot filter, a partition coefficient for a given  $i^{\text{th}}$  heavy metal in the ceramic candle hot filter may be defined as:

$$(x_f)_i = \frac{i^{\text{th}} \text{ HM content (wt.\%) in the flue gas after the filter}}{i^{\text{th}} \text{ HM content (wt.\%) in the fine fly ash (cake filter)}} \quad (2)$$

This coefficient is shown in Fig. 5 for Cd, Cu, Ni, Pb, Zn in three incineration tests with 0.03 wt.% Cl and in three other tests with 3.0 wt.% Cl in the feedstock, the other experimental conditions being the same. Conclusions that can be drawn from Fig. 5 are:

When the Cl-content in the feedstock was sub-stoichiometric:

- (1) the partition coefficients in the candle filter were below 0.02. This means that the hot filter retained more than 98 wt.% of the HMs in the flue gas.
- (2) In spite of the hot filter, the flue gas had HM contents higher than the targeted limits of the European Regulations. This means that another gas cleaning device has to be set downstream the hot filter.
- (3)  $x_f$  values were similar for all HMs considered here, there were no important differences between them.

When the Cl-content in the feedstock was over-stoichiometric,  $x_f$  values were

- for Cd and Pb: 2–3-fold higher than those obtained at 0.03 wt.%,
- for Cu, Cr and Zn: slightly higher than those obtained at 0.03 wt.%,
- for Ni: smaller than those obtained at 0.03 wt.%.

It may be concluded therefore that chlorine clearly affects the partitioning of Cd and Pb in the hot filter more than that of the other HMs studied, as Fig. 5 shows. This effect is

attributed to the fact that in these tests the content of HCl in the flue gas increased a lot. The gas face velocity was around 4 cm/s and the thickness of the cake filter was 1–4 mm. The residence time of the gas in the cake was only 0.02–0.10 s. This would be enough time to attack by HCl (at 750–760 °C, filter temperature) the ash on the filter surface and to form chlorinated volatile compounds (as CdCl<sub>2</sub> and PbCl<sub>2</sub>), which would bring such HMs from the cake to the flue exit gas. This fact agrees with the previous findings by Wey et al. [23] and Nieminen and Kurkela [65].

The decrease at high Cl-contents of the partition coefficient ( $x_f$ ) for nickel is not surprising. ClH does not attack, under these experimental conditions, to the nickel in the cake. The numerator of Eq. (2) does not increase for this element (Ni), thus. Nevertheless, most of the species in the cake filter are attacked by the ClH and are lost to some extent from that cake; the total amount of the other (not Ni)  $i^{\text{th}}$  species decreases, thus. The percentage (wt.%) of the Ni in the cake, the denominator of Eq. (2), increases then correspondingly, and it explains the decrease of the  $x_f$  coefficient for Ni under these experimental conditions.

## 5. Basic starting point for a model of the behaviour and partitioning of HMs in BFBs

From all existing data on incineration in BFBs, one important and basic fact is evident: for a given set of hydrodynamic conditions, the percentage of the different HMs, except Cd and Pb, is nearly the same in a given exit flow. For example, the partitioning of the HMs (except Cd and Pb) in our incineration test no. 27, with detailed experimental conditions given in [3], was:

- 24 ± 1 wt.% of each HM in the bottom ash,
- 40.5 ± 2 wt.% of each HM in the coarse fly ash,
- 33 ± 1 wt.% of each HM in the fine fly ash (cake filter),
- 0.8 ± 0.5 wt.% in the flue gas.

This partitioning changed if the hydrodynamic conditions were changed appreciably. For example, in the representative test no. 30, which is fully described in [3], the distribution of each (excepting Cd and Pb) of the HMs was as follows:

- 36 ± 4 wt.% in the bottom ash,
- 37 ± 5 wt.% in the coarse fly ash,
- 21 ± 8 wt.% in the fine fly ash (cake filter),
- 1 ± 0.5 wt.% in the flue exit gas.

Regarding the fate or partitioning of the HMs, it can be concluded that all HMs had the same fate, distribution or partitioning, except for Cd and Pb: the percentage of Cd and Pb were lower in the bottom ash and higher in the flue exit gas than the other HMs. Hence:

- *Except for Cd and Pb, all the HMs studied here had the same fate/distribution.*

- Cd and Pb contents in bottom ash were somewhat lesser than the other HMs.
- In the flue exit gas, and maybe also in the cake filter or fine fly ash, Cd is found in a higher amount/percentage than the other HMs.
- Pb has an intermediate behaviour between Cd and the others HMs studied here. The percentage of Pb in the fine fly ash is a little bigger than in the bottom ash, but not as much as in the case of Cd.

This behaviour of the HMs in BFBs incinerators is the same as the one reported by other authors ([9–13,32,54], etc.). In all cases, the concentration of a given HM (except for Cd and Pb) is nearly the same in the three exit flows of ashes.

## 6. Interpretation of results: fitting the partitioning to a conceptual model

All the above results can be explained with basic knowledge of chemical reaction engineering principles. The partitioning of the HMs is governed by the combination of kinetics and diffusion with fluid dynamics in the fluidized bed.

### 6.1. Kinetics of diffusion of the HMs in the particles

The average diameter of a particle of ash in the filter cake is around  $20\ \mu\text{m} = 20,000\ \text{nm} = 200,000\ \text{\AA}$ , and the average diameter of a particle of coarse fly ash is around  $200\ \mu\text{m} = 200,000\ \text{nm} = 2,000,000\ \text{\AA}$ . A particle of ash is  $10^6$  bigger than an atom of an HM since the diameter of an atom of one of these HMs is around  $1.5\ \text{\AA}$  (150 pm). The time needed for the atoms of a HM to diffuse by the solid matrix of the ash and to go out of the particle depends on the diameter and porosity of the particle of ash, the chemical composition of the matrix of the ash, the temperature, the volatility of the HM considered and so on. For example, the basic species of the ash matrix ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ) may react with the HMs encapsulating them towards the core of the particle, as Fig. 6a shows. The chemical composition of the matrix of the ash has a big influence on the vaporization kinetics of the HMs. The chemical composition also determines the binding force between the components of the ash and the HMs and the time required to diffuse the HM out of the particle.

The time to get an atom of HM out of the particle under incineration conditions is very difficult to calculate quantitatively. Nevertheless, there are the following experimental data regarding this matter:

- (1) In the extreme case of very big solid pieces, sometimes fed as full barrels in rotary kiln incinerators, this time is of a few hours [66].
- (2) Ludwig et al. [67], in their specific incinerator, needed more than 1 h to get the ash depleted of Cd and Zn.
- (3) Abanades et al. [41] using a BFB incinerator have recently calculated the time of vaporization of Cd, Pb and Zn. For cadmium, the most volatile of these HMs,

the average time for its depletion from the ash particles is in the range of 10–20 min.

That's to say, although there are no detailed studies on the kinetics of HMs vaporization from ash particles in BFBs under real incineration conditions, the recent works by Abanades and co-workers [41,42] indicate how the most volatile HMs, Cd and Pb, need at least 10 min to diffuse out of an ash particle of the size commonly found in fluidized bed incinerators. This figure will be further used for comparison purposes.

### 6.2. Kinetics of elutriation

Elutriation or carry over from BFBs is a very well known phenomenon, and deeply studied for many years. There is a huge number of papers published on the kinetics of elutriation in fluidized beds, even for the case of BFB incinerators [68]. From the lot of literature data to this concern, it is well known that the average residence time of the coarse and fine fly-ash particles in the bed of a BFB incinerator varies from a few seconds to a few minutes, depending mainly on the particle size, the  $[u_f/u_{mf}]$  ratio used, and on the total height of the bed. Concerning the freeboard of a BFB incinerator, the superficial gas velocity in the case of UCM's incinerator was 1.5–2.0 m/s and its height four meters. The average residence time of the coarse and fine fly-ash particles in that freeboard was therefore of only a few (2–4) seconds. The total or overall time for the elutriation or carry over of the coarse and fine fly ash generated in a BFB incinerator is in the range of some seconds to a few minutes, depending on the particle diameter of the ash. This time is much shorter than the time required for diffusing the HM atoms out of those particles.

Since the residence time of the coarse and fine fly ashes in a BFB incinerator is low, thus Cd, and Pb to a minor extent, only have time to be vaporized or lost in a fine outer shell of the ash particle (Fig. 6a). This amount increases the Cd content, and maybe also the Pb content, in the flue exit gas. The inner body of the particle remains homogeneously distributed along with the particle radius and only the outer part of the bottom ash particles can be depleted of these two HMs (Cd and Pb). However, the weight of the outer shell is not important with respect to the overall weight of the particle. Considering the overall weight of the bottom ash particle(s), only a small fraction of Cd and Pb is lost from those particles, as shown in Fig. 6a.

Given the very different times required for diffusion and elutriation in a BFB incinerator there is no time for a significant HM depletion, except for Cd, and to a minor extent for Pb, as proposed in Fig. 6b. The homogeneous distribution of the HMs in the particles remains the same in the 4 outlet flows of ash, except for Cd and Pb.

Since the HMs, except Cd and Pb, remain homogeneously distributed in the ash particles after incineration, their amount in each exit flow of ash will depend on the

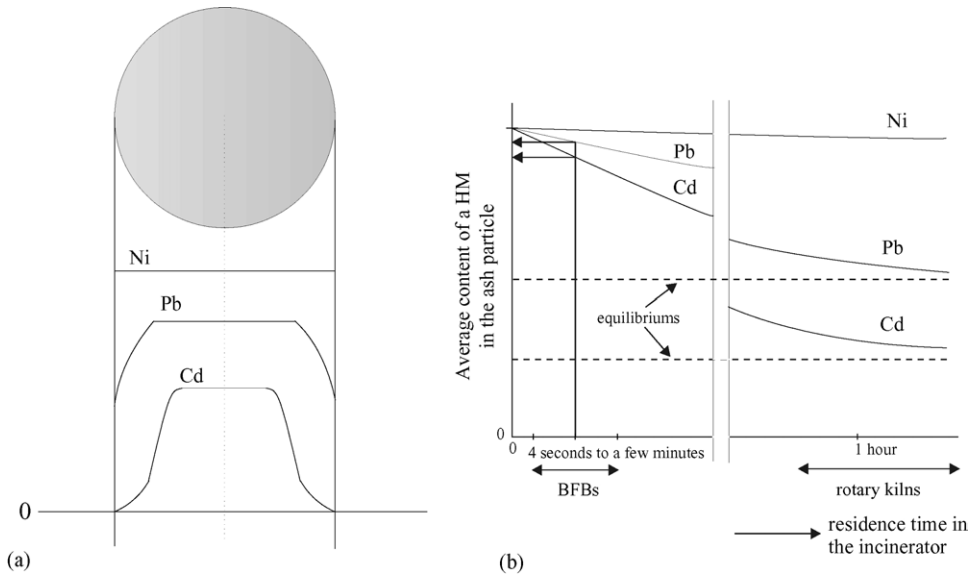


Fig. 6. Profiles of three (Cd, Pb, Ni) targeted HMs, rough estimates, according to existing data and for a given matrix of ash, incineration temperature and chlorine content in the incinerator. (a) Cross-section profiles in a particle of ash after a few minutes in the incinerator. (b) Averaged (with ash particle radius) content of the 3 targeted HMs in the particle of ash vs. residence time of the ash particle in the incinerator.

overall amount of each type of ash flow generated: bottom, cyclone or coarse, and cake filter or fine-ash flow. In a BFB incinerator these amounts are governed by the hydrodynamics in the incinerator, cyclone and downstream filter system. The “problem” of knowing the fate or partitioning of the HMs then becomes a problem of determining the amounts of the different ash exit flows, and it can be solved by using well known hydrodynamic principles.

### 6.3. Fluid or hydrodynamic aspects

The flows or amounts of ash leaving a BFB incinerator are governed by the basic principles of fluidization engineering [68,69]. In the incinerator used at UCM (Fig. 1) the freeboard is higher than the transport disengaging height (TDH). Fine and coarse ash particles are therefore not in packets or clusters, but isolated. Each particle has a terminal velocity,  $u_t$ , which depends on its size, density and shape. If  $u_t > u_f$ , such

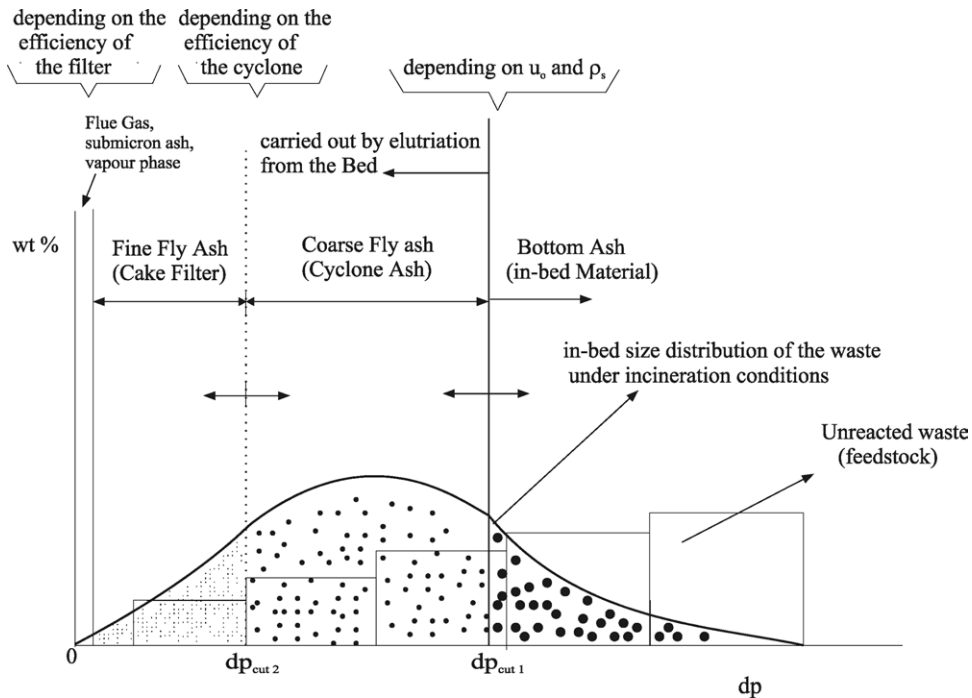


Fig. 7. Partitioning between the four exit flows of the solids generated in a BFB incinerator followed of a cyclone and hot ceramic filter.



an ash particle will fall down to the bed and will be collected as bottom ash. If  $u_t < u_f$ , such particle will be transported out of the incinerator (1st cut), as schemed in Fig. 7. The recent conclusions by Zhou et al. [42] concerning the hydrodynamics in a BFB incinerator fully agree with our results.

Downstream from the incinerator, in the cyclone, there is a ‘second cut’: the coarse fly-ash particles are collected at the bottom of the cyclone, and the fine fly-ash particles leave the cyclone and arrive at the surface of the hot filter. In the hot filter chamber there is a ‘third cut’: depending on the filtration characteristics, some fly ash will remain on the filter surface, as a cake, and the finest ones, mostly the submicron particles, plus the HMs in vapour phase, will go through the filter thus leaving in the flue exit gas.

Fig. 7 summarises these basic ideas. The ‘three cuts’ in the outlet flow of ash particles determine the amounts of the 4 outlet flows of HMs. And, these ‘three cuts’ are governed by the fluid dynamics in the incinerator, cyclone and hot filter.

Figs. 6 and 7 are drawings of the conceptual model proposed in this paper. These drawings are only qualitative because it was not possible to generate quantitative information from kinetics, diffusion and hydrodynamics calculations. Nevertheless, they were completely derived from the evidence of the experimental results. These figures are realistic, because they are based on all experimental data published on the fate of HMs in sludge and waste incineration. With this conceptual model and with the laws or principles which govern fluidization, cyclones and hot gas filtration, one should be able to calculate the amount of each HM which exits in each flow for a given set of experimental conditions in the FB incinerator, cyclone and hot filter.

## 7. Conclusion

The main conclusion of this work is that the amount of ash in the exit flows, and correspondingly the amount of each HM in each exit flow in a BFB incineration plant, is governed by: (1) fluid dynamics, (2) by the kinetics of diffusion of the HMs inside the ash particles, and (3) by the kinetics of the reactions of the HMs with the components of the matrix of the ash. In a BFB incinerator, the fine and submicron fly ashes do not have enough time of residence in the bed to reach the equilibria. Some thermodynamics calculations are not, therefore, very useful in BFB incinerators because equilibria are not reached in, at least, three, of the four existing, exit flows.

In rotary kilns and in grate systems, in which the residence time of the solids can be from half an hour to a few hours, the equilibrium between phases for each HM can be reached, as Fig. 6b shows. In a BFB the residence time of the fly ashes is some orders of magnitude (a few seconds compared to one hour) less than the one required to reach the equilibrium. HM partitioning does not therefore occur. The kinetics of diffusion of the HM inside the ash particle controls the fate of the HM in incineration in BFBs: *Most of the HMs have no time to diffuse out of the ash particle and remain in it.*

Such ash-particle will remain at the bottom of the bed, at the bottom part of the cyclone, or in the cake filter, depending on its diameter ( $d_p$ ), and on the fluid dynamics, design and operation of the incinerator, cyclone and filter. Except for Cd and Pb, there is no noticeable partitioning of HMs between the 4 exit flows in BFBs.

As a conclusion, the following can be said about a BFB incinerator:

- (1) The equilibrium, relating to the distribution of the HMs between phases, is not reached at all.
- (2) The distribution or fate of the HMs is absolutely governed by kinetics and by fluid-dynamic factors. Among these factors, the two most important ones are the superficial gas velocities in the incinerator and the particle size of the ash, which determines its ‘terminal velocity’,  $u_t$ .
- (3) The amount and/or percentage of chlorine in the feed-stock (in the interval of wt.% Cl studied here) has an important influence on the fate of specific heavy metals, like Cd and Pb.
- (4) Only Cd and Pb have some differences compared with the other heavy metals. The percentage/amount of Cd in the flue exit gas is higher than that of other HMs.
- (5) The partitioning of the HMs is different than the ones existing in other types of incinerators. The fate of the HMs depends on the residence times of the ashes and/or particulates at high temperature, and these residence times are or may be very different from one incinerator type to another one.

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