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# Behavior of heavy metals in the combustion gases of urban waste incinerators

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method of samples from the second clarifier outlet may be proposed:

(1) Samples should be chilled to near 0 °C and stabilized with 4% (w/w) sodium azide immediately after sampling. This minimizes the biodegradation of surface-active pollutants over 2-3 days.

(2) Either the standard measuring technique (defined time schedule for drop formation) or the equilibrating measuring technique (self-adapting time schedule) can be used to obtain reproducible surface tension values.

(3) Surface tension data reported for experiments carried out either by the standard or by the equilibrating measuring technique should include the information on the drop formation times.

(4) In practice, a preliminary standard technique experiment with 15-20-min drop formation time should be made (step A).

If a surface tension value of  $\leq 65$  mN/m is obtained in step A, a second standard experiment with tripled drop formation time should be carried out, which then will produce a near-equilibrium value.

If a value above 71 mN/m is obtained in step A, no further action is required for pollution control purposes.

If a value between 65 and 71 mN/m is found in step A, then a further experiment with tripled drop formation time should be made in order to decide whether an equilibrating experiment is required. The latter is required if the surface tension of the former experiment is within 2 mN/m of the legal limit (60 mN/m for urban wastewater treatment in Switzerland).

(5) Automatization of both measuring techniques is essential in applications to polluted wastewaters.

The procedures might also be used for the determination of biodegradation kinetics of surface-active solutes in aqueous media.

## Acknowledgments

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Registry No. Water, 7732-18-5; sodium azide, 26628-22-8.

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# Behavior of Heavy Metals in the Combustion Gases of Urban Waste Incinerators

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■ The behavior of each of the principal heavy metals present in fly ash from urban waste incinerators is described on the basis of the standard free energies of formation of the oxide and the chloride from the metal, oxygen, and hydrochloric acid, as well as the vapor pressure of the chlorides at working temperatures. The thermodynamic parameters are correlated with the three types of behavior in the volatilization process. The solubility in acid aqueous medium is also related to the oxide and chloride thermodynamic parameters. A correlation has been established between the amount of each heavy metal in the fly ash and the standard free energy of vaporization of its chloride, both in the samples used and in the data on content found in the literature. Finally, kinetic modeling studies have been used to show that the neutralization of the fly ash alkalinity takes place by a diffusion mechanism through a solid matrix.

## Introduction

The treatment of urban waste by incineration makes it possible to obtain energy from this waste while reducing

its volume by a large amount. In addition, the dumping of combustion ash is much less conflictive than the dumping of nonincinerated waste. These attractive aspects of the process have extended its application and, consequently, augmented the interest in studies on its environmental implications.

The presence of heavy metals in urban waste combustion gases has been a subject of particular interest. The incineration of solid waste contributes significantly to the presence of Cd, Zn, and Sb and possibly Ag, In, and Sn in urban area aerosols (1, 2). Mercury is capable of passing through the gas treatment system, generating emission levels of the order of 0.05-1 mg/Nm<sup>3</sup> (3). A review of the available literature leads to the conclusion that the release of heavy metals has been clearly established, both in the combustion of fossil fuels in general and in the burning of urban waste (4-7). Another basic aspect of the burning of organic matter of any origin is the presence of SO<sub>2</sub>, HCl, and oxides of nitrogen in the combustion gases. The hydrochloric acid present in urban waste combustion gases comes from the burning of plastics—especially polyvinyl chloride—and its concentration in the gases increases along

with the proportion of plastic in the waste. The interrelation between the volatilization of heavy metals and the presence of HCl in combustion gases has already been noted by some authors (1, 8).

Cahill and Newland (8) have proposed a volatilization-condensation mechanism based on the observation that the heavy metals present in the fly ash are found on the ash surface in the case of metals with compounds whose boiling or sublimation temperature is less than 1823 K. They have compared the volatility of oxides, chlorides, sulfides, and the elements themselves and have reached the conclusion that, as postulated by Davison et al. (9), the primary factor that determines when a metal is present in the matrix of the ash particles or on their surface is its boiling point. This explanation is in accordance with the classification of chemical elements in terms of their relative enrichment in fly ash as proposed by Klein et al. (5):

**Class I: Al, Ba, Be, Ca, Co, Fe, K, Mg, Mn, Si, Sr, and Ti.** Elements with high boiling points that are not volatilized in the combustion area. They make up the matrix of fly ash and are deposited only minimally on the surface.

**Class II: As, Cd, Cu, Ga, Pb, Sb, Zn, and Se.** Elements that are volatilized during combustion, with very little chance of remaining in the bottom ash. When the combustion gas stream cools down, the compounds of these metals condense on the surface of the fly ash particles. Ontiveros et al. (10) have shown how the concentrations of these metals become higher as the fly ash particle size diminishes.

**Class III: Hg, Cl, and Br.** These remain in gas phase throughout the entire process. They undergo volatilization but not condensation.

**Class IV.** This includes elements whose behavior is a combination of two or more of the above three classes.

Cahill and Newland modified the Klein classification according to their analytical results, although their observations fundamentally agree with Klein's: Some elements present in fly ash are found in the particle matrix and have been transported mechanically by the gas stream; others undergo some sort of volatilization followed by condensation as the combustion gases cool down. This condensation cannot be complete, and at least some of them are given off into the urban atmosphere where they may remain in the form of aerosols. Finally, a third group undergoes volatilization, but the output temperature of the gases in the purification system does not allow them to condense and a large proportion of them are given off into the atmosphere.

Greenberg et al. (1) have indicated the possible effects that the presence of high HCl concentrations in the gas stream may have on the volatilization of heavy metals. The HCl concentration in urban waste combustion gases is of the order of  $10^2$ – $10^3$  mg/Nm<sup>3</sup> and, therefore, sufficiently high to enable the formation of metal chlorides in the combustion chamber. They found chloride concentrations of the order of 14–20% in fly ash, a sufficient amount to provide anions for most of the heavy metals present in the ash. They also indicate that a complete understanding of the transport mechanisms is more complicated since, for example, aluminum and iron form volatile chlorides but are not particularly concentrated in fly ash, whereas silver, which has no volatile compounds, does concentrate.

A better understanding of the distribution of these heavy metals in fly ash and the mechanism by which they are transported in the combustion gas stream could be a solid basis for the development of mechanisms for controlling

the resulting pollution. No less important is the study of dissolution mechanisms in water because of their special significance for making fly ash inert or utilizing it. This study attempts to clarify the transport mechanism of heavy metals by the combustion gas stream on the basis of available data on the composition and structure of fly ash, by providing an analysis of the thermodynamics of the possible processes. These mechanisms are discussed in relation to the processes for dissolution of heavy metals in water.

The possibilities for combination of the heavy metals present in fly ash have been discussed by numerous authors. Cahill and Newland (8) mentioned the possibility that heavy metals may be found in elemental form or in the form of oxides, sulfides, or chlorides. Greenberg et al. (1) have found the following elements associated with the smallest ash particles which undergo volatilization-condensation: Na, Cl, Br, Cu, Zn, As, Ag, Cd, In, Sn, Sb, W, and Pb. They stated that a possible effect of high concentrations of chlorine compounds in the combustion gas stream may be the formation of chlorides of Pb, Sb, Cd, As, Zn, and Ni, whose boiling points are below 1273 K. However, they considered that it is inconsistent with this hypothesis that Fe and Al, which have low boiling point chlorides, do not concentrate on the outside of the particles and therefore would not undergo volatilization-condensation. Silver, on the other hand, which has no volatile compounds, does concentrate on the surface; they therefore concluded that the complete explanation is more complicated.

Ontiveros et al. (10) stated that Na and K are found mainly as chlorides. The chloride concentrations in the ash of different origins studied by this group were between 1.9 and 5.2%. The principal anions they found were chlorides and sulfates in sufficient concentrations to satisfy the charge balance with sodium, potassium, and calcium.

The formation of heavy metal chlorides, followed by their distillation, is a common process in the field of metallurgical engineering. This was one of the most used processes for eliminating heavy metals from iron ores (11). A fundamental difference between iron ore and urban waste in terms of the presence of heavy metals is that they are usually found in the form of oxidated compounds in ores, while in urban waste they usually occur in elemental form, either pure or in alloys with other metals. For extracting heavy metals from ores, chlorine must be added since the ore does not contain sufficient amounts of it; this is usually done in the form of CaCl<sub>2</sub>, Cl<sub>2</sub>, or HCl. In the burning of urban waste, the presence of HCl in the combustion gases has been clearly established and may spontaneously cause the same chemical reactions that take place in certain metallurgical processes used for extracting heavy metals. For this reason, the thermodynamics of chloride formation from oxides and chlorine gas have already been studied (12). In our case, the situation is different since the metals are most commonly found as elements, and chloride formation requires a metal, atmospheric oxygen, and HCl.

### Materials

The ash samples used in this study were taken from the Barcelona urban waste incineration plant between January and July 1990. In 1989 this plant treated 258 000 tons of urban waste and produced electric power (94 900 MWh), scrap iron (7530 tons), and 67 040 tons of ash, of which approximately 3000 were fly ash collected by electrostatic filters (13).

The three rocking grates of the primary combustion chamber of the incinerator plant are fed by a large hopper

**Table I. Concentrations in Ash from the Barcelona Urban Waste Incinerator Plant**

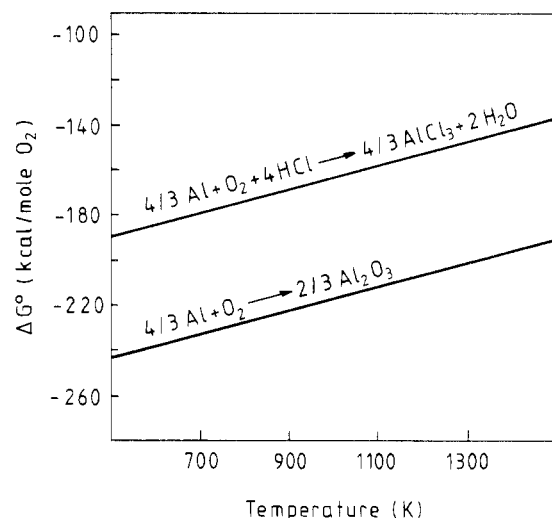
element/ ion	concentration, $\mu\text{g/g}$			
	sample 1		sample 2	
	av	range	av	range
Zn	14 800	10 800–15 300	33 200	30 000–35 700
Pb	10 020	8 760–11 900	20 800	18 400–22 100
Cu	1 400	1 100–1 630	2 700	2 500–2 850
Cd	400	200–600	800	650–1 050
Ag	40	5–70	220	100–300
Al	60 120	58 200–62 300	11 360	10 000–13 400
Ti	7 500	6 800–8 100	2 160	1 900–2 300
Cr	580	340–770	340	180–400
Fe	9 400	8 300–10 000	11 400	10 200–13 000
Sn	3 300	2 750–4 100	4 600	3 900–5 200
Mn	1 200	950–1 300	500	350–700
Sb	240	150–300	650	550–750
Ni	58	25–70	39	20–55
Ca	119 100	118 000–123 000	33 200	30 500–35 000
K	77 000	74 800–82 000	130 000	125 000–136 800
Na	59 300	57 800–62 000	113 700	111 900–115 600
Mg	9 400	8 600–10 300	2 900	2 690–3 200
Ba	1 200	1 050–1 400	710	550–900
Br	380	290–420	320	250–350
Rb	150	80–190	250	210–290
V	40	10–60	8	0–15
Ce	32	15–45	9	0–15
As	25	12–39	33	22–44
Mo	25	10–42	23	19–33
Co	16	6–27	9	0–18
La	15	3–29	4.2	0–7
Se	13	0–20	22	16–31
Nd	13	2–18	5	0–8
Cs	11	3–19	19	10–23
W	13	5–21	17	5–21
Th	3.7	0–5	<0.2	
Tl	2	0–5	8	0–12
U	1.9	0–3	<0.7	
Hg	1	0–3	4	0–6
Sm	1.8	0–3	0.4	0–1
Te	0.5	0–1	0.8	0–1
CO <sub>3</sub> <sup>2-</sup>	60 000	57 300–62 450	<100	
SO <sub>4</sub> <sup>2-</sup>	190 000	182 000–199 650	480 000	455 000–500 000
SO <sub>4</sub> <sup>2-a</sup>	17 000	12 600–21 350	74 000	68 750–82 235
Cl <sup>-</sup>	106 000	100 675–112 358	56 000	48 670–62 340
insol <sup>b</sup>	251 190	245 345–276 874	61 500	55 350–66 345

<sup>a</sup> Water soluble. <sup>b</sup> Insoluble in 3 M HCl.

using an electrohydraulic grab. Fuel injection is not needed as the waste residues burn without external aid. After the combustion process, the hot residues are dropped into a water-quench tank. After quenching, the residues are carried by drag conveyor to a chute for loading onto disposal trucks.

The combustion gases leave the oven at a temperature of  $\sim 1200$  K. The gases are cooled to about 600 K in the tubular heat exchangers, and finally the fly ash particles are collected by electrofilters of two fields, with a collection efficiency of 98%. Thus, the amount of suspended particles is reduced from 5 to 0.1 g/Nm<sup>3</sup>. The electrofilters are cleaned every 45 days. Residence times for gases and solids are 0.3 and 90 min, respectively.

We worked essentially with two kinds of samples to obtain information on the composition of fly ash and its chemical reactions. The first, called sample 1, was considered to be representative of the fly ash coming from both fields of the electrofilter in plant operation and had the mean composition of 15 samples of 1 kg taken periodically (every 12 days; when the plant stopped for maintenance the correspondent sample was taken 15 days after the last one). The samples were taken from the two fields of the electrofilters and mixed. The second, termed

**Figure 1.** Standard free energy of reactions forming aluminum oxide and aluminum chloride versus temperature (calculated with ref 15).

sample 2, was taken from the fly ash encrusted on the stationary parts of the electrofilters, which are removed periodically during maintenance shutdowns. This latter sample presents a contact time with the combustion gases of the order of several months. Comparison with sample 1 gave us information on the chemical reactions that take place in fly ash, once in the electrofilters, since their effects will appear more extensively than in sample 1, whose contact time with the gas stream is around 30 s.

Table I gives the concentration ranges of the two kinds of sample studied.

Instrumental neutron activation analysis (INAA) was used, along with inductively coupled plasma (ICP) and atomic absorption spectrophotometry (AAS) from solutions obtained by strong acid digestion [with aqua regia/HF and HF/HClO<sub>4</sub> (8)], which dissolved the sample almost totally, releasing the heavy metals from the matrix for determination of the total metal concentrations. The standard addition method of analysis was used.

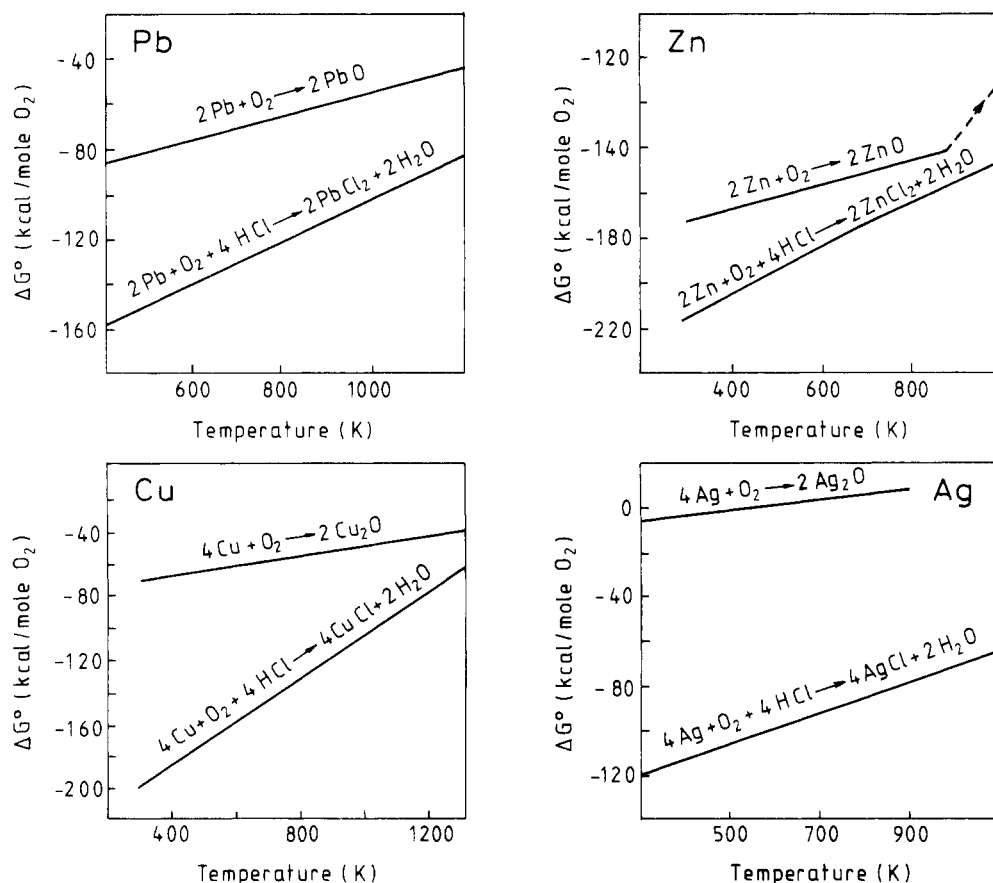
Carbonates, chlorides, and sulfates were determined by the usual gravimetric methods.

These results are in agreement with those obtained previously by other authors in order of magnitude (1, 10, 14). Ontiveros et al. (10) looked at heavy metals in fly ash of six different origins and concluded that, in general, the fly ash metal concentrations fell within a close range.

### Results and Discussion

In order to understand the different behavior patterns of the chemical elements present in fly ash in the combustion gas atmosphere in the presence of hydrochloric acid and oxygen, we used the available thermodynamic data (15, 16) to determine the standard free energy of reaction ( $\Delta G^\circ$ ) as a function of temperature for the oxide-forming reactions and for the chloride-forming reactions involving the metal, HCl, and oxygen, at the habitual temperature ranges in the combustion chamber and in the electrostatic filters or collectors. The resulting diagrams show the presence of three clearly different situations, which correspond directly to the three basic groups of behavior patterns established by Klein (5) and by Cahill and Newland (8).

The first group of elements presented a  $\Delta G^\circ$  value for the reaction to form the oxide from the metal plus oxygen that was much higher at all temperatures than the  $\Delta G^\circ$  value for forming the chloride from the metal, oxygen, and hydrochloric acid. These are basically the class I elements from Klein's classification. Aluminum is a clear example,

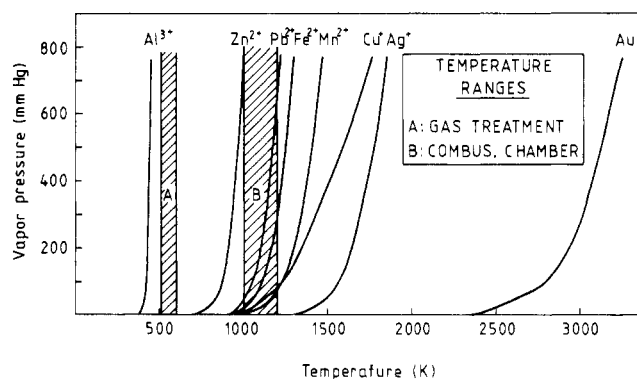


**Figure 2.** Standard free energy of reactions forming oxides and chlorides of silver, lead, copper, and zinc versus temperature (calculated with ref 15).

as can be seen in Figure 1. Since the oxide is much more stable than the chloride at any temperature over the range under study, it is to be expected that aluminum will remain in the combustion chamber in the oxide form, if it enters as such. Metallic aluminum will undergo oxidation on the surface or may melt, but the volatilization-condensation of its chloride is not possible since the latter does not form.

The second group of elements showed a greater tendency toward the spontaneous formation of the chloride rather than the oxide at all temperatures of the combustion and gas filtration cycle. Figure 2 shows the thermodynamic situations of Pb, Zn, Cu, and Ag as examples. The most stable combination form for these elements in the combustion gas stream is as chlorides, and it is to be expected that they will be transported in this state. The boiling points for the chlorides in this group of metals are less than 1823 K and also lower than the usual temperatures in the combustion chamber (1123–1273 K). Their vapor pressures are high enough so that large amounts of them can be transported to the gas treatment systems where the temperature is usually much lower (Figure 3).

There is a third group of elements for which the relative stability is not so clearly defined as for the two preceding groups because the increments of free energy for the formation of their oxides and chlorides under standard conditions are similar or because they can exist in more than one state of oxidation, giving rise to somewhat more complex situations. Examples of this group are Fe and Mn, whose diagrams are given in Figure 4. When, as in the case of manganese, the oxide- and chloride-forming lines are close together, it is to be expected that the total amount of the element in the fly ash is divided up between the two compounds and distills only partially, since the vapor pressure of the oxide is too high for the element to be

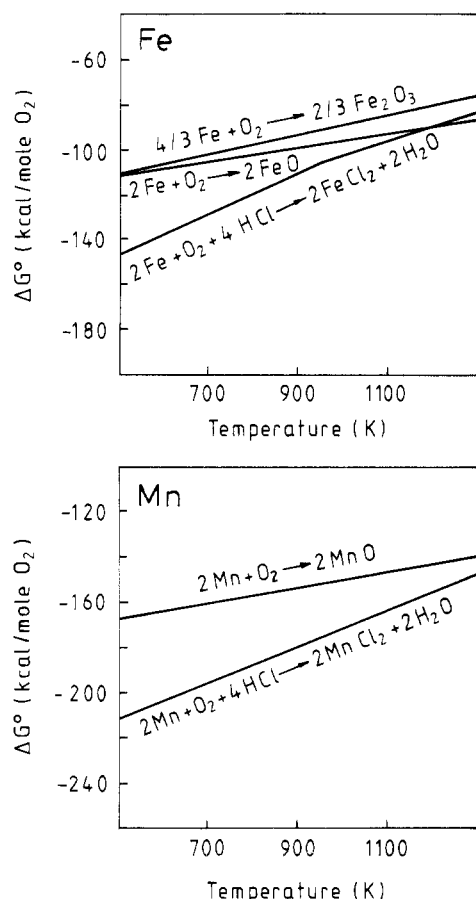


**Figure 3.** Vapor pressure of the chlorides studied, and of gold in elemental state, versus temperature (taken from ref 16).

transported as oxide in its gaseous form. In sample 1 only 20% of the total manganese was soluble in dilute sulfuric acid, leading to the conclusion that the rest was present in oxide form, probably inside the matrix of the ash particles carried by the gas stream to the electrofilters.

Iron also presents a complex situation. The chloride of  $\text{Fe}^{3+}$  is not stable at temperatures above 633 K. The only way for iron to form a volatile compound is by forming the chloride of  $\text{Fe}^{2+}$ . The possibility of iron occurring at its lower valence depends on the composition of the combustion gas stream. An excess amount of air will prevent Fe distillation, while a reducing atmosphere will favor the formation of  $\text{Fe}^{2+}$  and the subsequent formation of volatile ferrous chloride. For iron then, we can expect a similar behavior to that of manganese.

If the basic mechanism for transporting a metallic element is chloride formation-volatilization-condensation, the relative amount of each heavy metal subject to this



**Figure 4.** Standard free energy of reactions forming oxides and chlorides of manganese and iron versus temperature (calculated with ref 15).

process present in the ash must be directly proportional to the difference of its chloride's partial pressure between the temperature in the combustion chamber and that of the gas filters. Figure 5 shows a linear relation (correlation coefficient 0.982) between the mass percentage of each of the heavy metal chlorides of sample 1 and the difference between the vapor pressures of its chloride at 1200 K and 600 K. Similar results are obtained if we plot data at 500 K instead of 600 K, because the vapor pressures at 1200 K are usually many orders of magnitude greater than vapor pressures at the electrofilter temperature.

If we use  $Q$  to designate the combustion gas flow rate and  $n$  for the number of moles of chloride formed, transported, and condensed in the ash filter, we can use the following formula for each of the chlorides present in the combustion area

$$P_{vc}Qt = n_cRT_c \quad (1)$$

where  $P_{vc}$  is the vapor pressure of the chloride,  $t$  is time,  $n_c$  is the number of moles of metallic chloride in the vapor phase, and  $T_c$  is the temperature in the incinerator furnace.

At the filter temperature

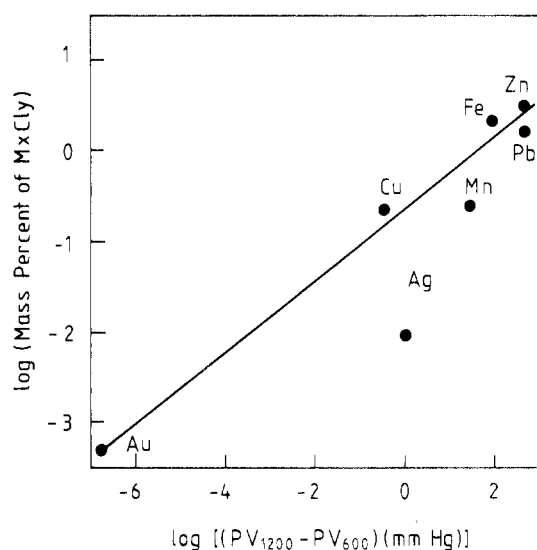
$$P_{vf}Qt = n_fRT_f \quad (2)$$

with  $P_{vf}$  and  $n_f$  representing respectively the vapor pressure and the number of moles of metallic chloride at the filter temperature ( $T_f$ ).

The number of moles of chloride transported will be

$$n = n_c - n_f = \frac{P_{vc}Qt}{RT_c} - \frac{P_{vf}Qt}{RT_f} \quad (3)$$

$$= Qt/R[(P_{vc}/T_c) - (P_{vf}/T_f)] \quad (4)$$



**Figure 5.** Logarithm of mass percent of metal chloride, in sample 1, versus logarithm of the difference in chloride vapor pressures, taken from ref 16, at 1200 and 600 K.

provided that the amount of heavy metal present in the burning residue is enough to satisfy this expression.

If the vapor pressure at the filter temperature is low enough, this situation can be written as follows:

$$n = kP_{vc} \quad (5)$$

The vapor pressure of the chloride and the temperature are related to the standard free energy of vaporization ( $\Delta G^\circ_v$ ):

$$\Delta G^\circ_v = -RT \ln P_{vc} \quad (6)$$

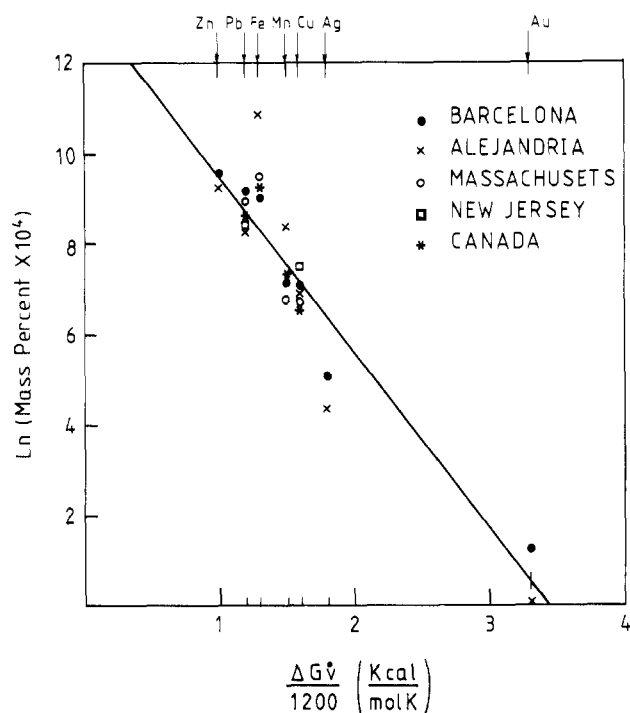
$$n = k \exp(-\Delta G^\circ_v/RT_c) \quad (7)$$

Taking logarithms of both members of eq 7, we have

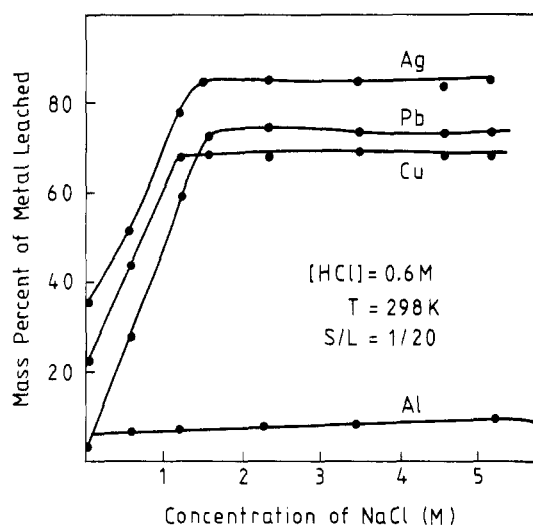
$$\ln n = \ln k - (\Delta G^\circ_v/RT_c) \quad (8)$$

Further, if the various combustion temperatures given in the literature are not very different, a plot of the Napierian logarithm for the metallic chloride contents in the ash against  $\Delta G^\circ_v/T$  should be a straight line. Figure 6 shows the Napierian logarithm for the mass percent of each metal compared with the term  $\Delta G^\circ_v/1200$  for each heavy metal analyzed. We consider 1200 K as the temperature most commonly occurring in the combustion chamber. There is good linear correlation between the two parameters (correlation coefficient = 0.939), even though the analytical data come from plants of clearly different design. We can therefore conclude that the formation-volatilization-condensation of chlorides plays an important role in the transport of heavy metals by the combustion gas stream.

The relative position of the  $\Delta G^\circ/T$  lines from the oxide- and chloride-forming reactions also plays an important role in the solubility shown by the different heavy metals in acid aqueous medium. The presence of lead and silver in the samples studied will require the use of some complex-forming agent to solubilize them, since their chlorides and sulfates are fairly insoluble. We studied the effect of the chloride concentration on the solubility of Pb and Ag in aqueous phase and found a marked effect on copper solubility. Figure 7 shows the amount of metal leached at 298 K as compared to the chloride concentration of the solution when the initial HCl concentration was 0.6 M and the solid/liquid ratio in the pulp was 1/20. The silver,



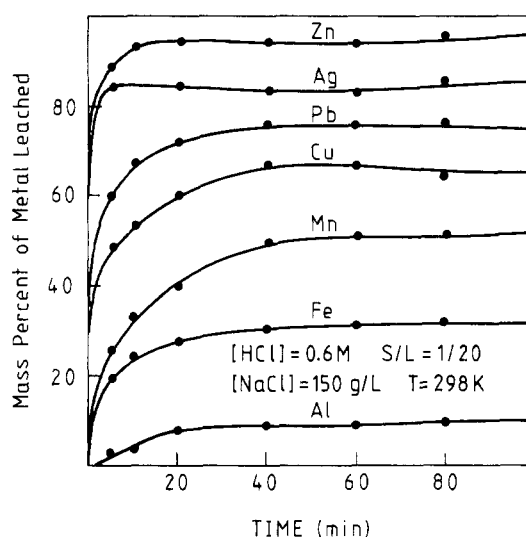
**Figure 6.** Napierian logarithm of mass percent of metal versus standard free energy of vaporization divided by 1200 K for five Incinerators: Barcelona, Alejandria (taken from ref 11), Massachusetts, New Jersey, and Canada (taken from ref 10).



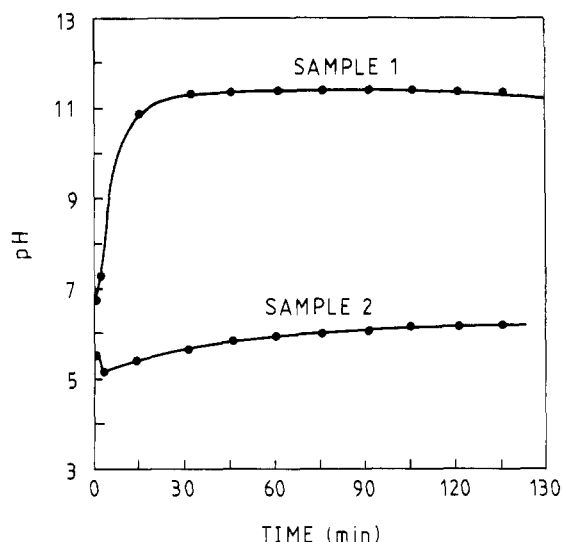
**Figure 7.** Effect of chloride concentration on the solubility of silver, lead, copper, and aluminum. Sample 1 (experimental values).

lead, and copper all became considerably more soluble by increasing the chloride concentration. The marked effect on the solubility of copper indicates that most of it was present in the form of  $\text{Cu}^+$  compounds.

We used a solution containing a sufficient chloride concentration to solubilize silver, lead, and copper (150 g/L) to look at the solubility of the different elements in aqueous medium with a 0.6 M HCl concentration at 298 K. The results are given in Figure 8, which shows that the water solubility of the different elements is related to the thermodynamic situation described in Figures 1, 2, and 4. As the oxide becomes more stable than the chloride in combustion-chamber conditions, the solubility of the element in question decreases, since it must remain in the fly ash in the form of an oxide or oxidated compound, such as silicates, which have been carried along by the combustion gas stream. Their presence inside the matrix



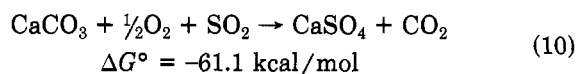
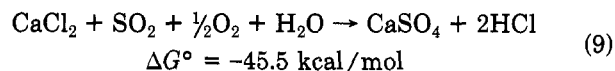
**Figure 8.** Effect of leaching time on the solubility of different heavy metals present in sample 1 (experimental values).



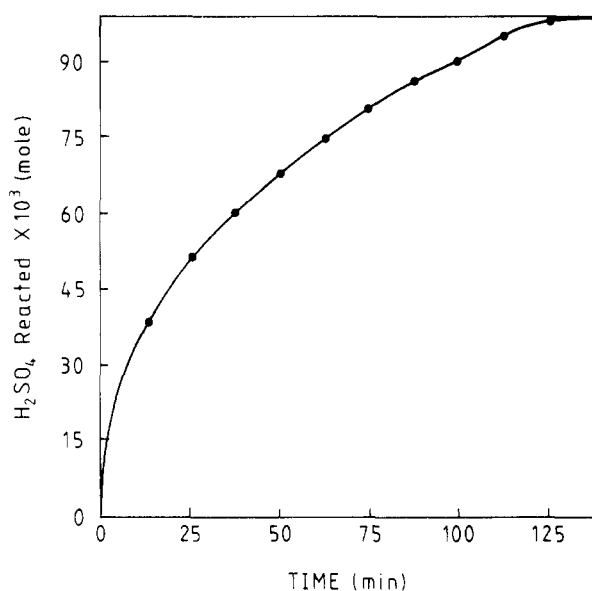
**Figure 9.** pH/time curves obtained by placing 10 g of fly ash in 100 mL of water for the two samples studied (experimental values).

means that longer reaction times or much higher acid concentrations are required for dissolution.

The composition of the two samples mentioned above and their different behavior in aqueous medium gives us more information about the reactions occurring in the combustion furnace. Figure 9 gives the pH/time curve resulting from the pH measurement of a suspension made up of 10 g of fly ash in 100 mL of water. The pH of sample 2, whose contact time with the combustion gas flow is very long, was considerably lower than that of sample 1. A prolonged contact time with the combustion gas stream eliminates the carbonates and increases the sulfate concentration. We also noted a drop in the total chloride concentration. Therefore, spontaneous reactions are taking place between the gas phase and the solid phase at 773 K, as follows:



Similar reactions with the carbonates of alkaline metals are also spontaneous at these temperatures. These reac-



**Figure 10.** Volume of  $\text{H}_2\text{SO}_4$  consumed to maintain the pH at 4 versus time in 300 mL of pulp with a solid/liquid ratio of 1/5. Sample 1 (experimental values).

tions are probably responsible for the reduction in the carbonate and chloride content and for the increase in the sulfate concentration as the contact time with the gas stream increases.

The following experiment was performed to determine whether the fly ash alkalinity neutralization reactions in aqueous medium are controlled by the chemical reaction on the particle surface or by diffusion through the insoluble matrix: 60 g of fly ash was placed in 300 mL of water and kept in suspension by magnetic stirring. The pH was kept constant at 4 by adding 0.9 M  $\text{H}_2\text{SO}_4$ . Figure 10 shows the amount of added  $\text{H}_2\text{SO}_4$  plotted against the contact time.

If the speed at which sulfuric acid becomes neutralized is determined by the reaction rate on the solid particle surface, then the following must be true (17):

$$1 - (1 - X)^{1/3} = kt \quad (11)$$

whereas if the neutralization takes place at a rate controlled by diffusion through the porous matrix, the following should hold

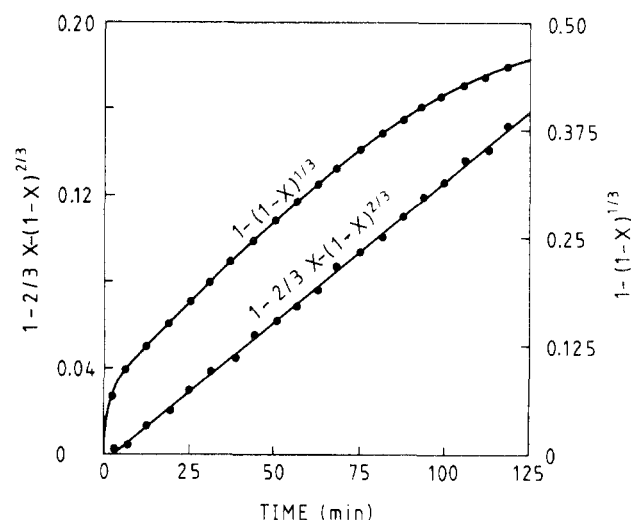
$$1 - \frac{2}{3}X - (1 - X)^{2/3} = kt \quad (12)$$

where  $X$  is the fraction reacted, i.e., the volume of  $\text{H}_2\text{SO}_4$  solution used at each different period of time, divided by amount of acid used at the end of the neutralization.

Figure 11 is a plot of the term on the left of eqs 11 and 12 against time for the two models described in these equations. When a given model is satisfied we obtain a straight line, and this result comes about only in cases where we assume control of the process by diffusion through the porous matrix. The compounds that are transported mechanically are found in the matrix of the particles; their dissolution in acid medium, keeping a constant pH, is controlled by diffusion and requires longer times than those needed to leach the heavy metals transported by volatilization-condensation, which are found on the surface of the particles that need short times to be dissolved.

### Conclusions

Three different relative stabilities are possible for a heavy metal compound present in the incineration of urban waste, depending on the thermodynamic stability of its oxide being greater than, equal to, or lower than its chlo-



**Figure 11.** Kinetic model trial, surface chemical reaction and diffusion through a solid matrix (experimental values).

ride. If the oxide is more stable than the chloride, the element is transported mechanically and is found in the matrix of the fly ash particles giving them alkalinity. The elements whose oxides and chlorides present similar stabilities are transported by both volatilization-condensation and mechanical mechanisms. When the chloride is more stable than the oxide, the heavy metal chloride is transported principally by volatilization-condensation, is deposited on the surface of the fly ash particles, and consequently, forms compounds with high solubility.

The percentage of this latter elements in fly ashes from different plants is directly correlated with the difference of vapor pressure of their chlorides between the combustion furnace and the electrostatic scrubber. Since they are combined as soluble chlorides like Zn, for example, or as insoluble chlorides that form soluble complexes, if an excess of  $\text{Cl}^-$  is present, like  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Pb}^{2+}$ , they can be dissolved rapidly at low pH or at high chloride concentrations in water.

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