

# Equilibrium analysis of the affect of temperature, moisture and sodium content on heavy metal emissions from municipal solid waste incinerators

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## Abstract

An equilibrium analysis was performed to determine the impact of the variations in the moisture and sodium contents in the solid waste feed on heavy metal speciation in municipal solid waste (MSW) incinerators. This analysis was based on the speciation of heavy metals among chlorides, oxides and other species under various incinerator conditions. The Gibbs free energy of the reaction mixture was minimized by the method of chemical potentials combined with atom population constraints using a thermodynamic equilibrium computer code. Fifty eight species were considered, including compounds of six trace metals, aluminum, cadmium, chromium, mercury, sodium, and lead. Changes in the moisture and sodium contents in the feed waste were found to significantly impact the speciation of heavy metals among chloride and oxide species. Estimates have been carried out on the impact of these speciation changes on the bottom ash, fly ash and flue gas emissions of heavy metals. The results indicate that, at the typical municipal incineration temperature of 950°C, a decrease in the waste moisture content from 37% to 5% results in a modest increase in the percentage of the lead in the fly ash from about 54% to 68% of the total. Similarly, a decrease in the waste sodium content from 6560 ppm (upper limit for MSW content) to 4500 ppm (MSW average) results in a more significant increase in the percentage of lead in the fly ash from 36% to 60% at the average waste moisture content. Several other heavy metals have also been studied, but the impacts are much smaller. A qualitative discussion and resulting

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implications of environmental impact due to the shifts in lead speciation are discussed. © 1997 Elsevier Science B.V.

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## 1. Introduction

Incineration is currently the focus of much research and regulatory effort, due in part to the emissions of heavy metals and organic combustion byproducts, especially chlorinated organics. While incineration is an effective tool for the integrated management of municipal solid wastes (MSWs), especially to reduce the volume and biological activities, the environmental acceptability of the emissions from MSW incineration is a major concern in the operation of the incinerator. Better understanding of the chemical and physical processes that result in the emission of heavy metals and organic compounds will lead to better methods of post-combustion control and potentially methods to reduce the production of organic pollutants in the combustion process itself. The speciation of heavy metals can affect aerosol formation processes, determining to some extent whether these compounds become part of the fly ash or remain in the gaseous phase [1,2]. This, in turn, influences the efficiency of removal of these heavy metal species before they leave the incineration system.

Atmospheric emissions of heavy metal species from municipal incineration plants depends not only on its combustion conditions, but also on the chemical reactions that determine the distribution of these heavy metals among the relevant chemical species. A few chemical reactions that affect the speciation of lead are:



In this work, an equilibrium analysis of the incineration system has been carried out using the method of element potentials in combination with atom population constraints to minimize the Gibbs free energy of the entire reaction system. Wu and Biswas [3] and Wu et. al. [4] used a similar methodology and performed equilibrium analyses of the speciation of heavy metals at nominal waste moisture in municipal solid waste incineration. These two previous studies analyzed the effect of temperature and chlorine content on the heavy metals speciation (chlorides vs. oxides). Wu and Biswas [3] found that most of the chlorine (98%) combines with hydrogen to form HCl due to the excess amount of hydrogen available in the combustion mixture. For heavy metals, Wu et al. [4] reported that lead and arsenic exist in the incineration system primarily as chloride species, while mercury and cadmium were found to remain mostly in their elemental forms.

Inspection of the reactions listed in Eq. (1) indicate that waste moisture in the incineration waste feed should play an integral part in determining the speciation of heavy metals in the incineration reaction system. This is because water impacts directly

the equilibrium between Cl and HCl and between the chlorides and oxides of heavy metals. Changes in waste moisture content can also lead to change in the incineration combustion temperature unless the latter is actively controlled by adjusting the excess air. In addition, other waste components such as alkali metals may also have an impact on the speciation of heavy metals because they have a greater affinity for binding with chlorine than hydrogen. Furthermore, alkali metals such as sodium may even combine chemically with chromium to form  $\text{Na}_2\text{CrO}_4$  in the reaction mixture. So the impact of sodium on chromium speciation should be even more significant than suggested by the equilibrium reactions in Eq. (1). In the previous studies of Wu and Biswas [3] and Wu et al. [4], the average waste moisture content of 25% and the average sodium content were used for the incineration waste feed. The role of waste moisture and sodium content on heavy metals emissions was not studied.

Considerable variations in the composition of MSW feed is expected to occur due to natural variations in the waste stream. For example, the moisture and sodium contents in the municipal solid wastes can vary significantly due to ‘pulses’ of waste components such as yard wastes and food wastes. In addition, municipal solid waste management practices to remove yard and food wastes from the municipal solid waste stream for composting may also reduce the waste moisture content. In this study, equilibrium analyses are expanded from the previous studies of Wu and Biswas [3] and Wu et al. [4] to account for the variations in waste moisture and sodium contents. The chloride–oxide speciations of 4 heavy metals (Pb, Cr, Cd, Hg), are examined as a function of the waste moisture content from a thermodynamic equilibrium viewpoint. The impact of the sodium content in the waste stream has also been investigated. These thermodynamic equilibrium analyses can help illustrate the trends in heavy metal speciation when the waste moisture and waste sodium contents are varied. These speciation estimates can provide the basis for more detailed investigations of the pollutant formation process, including physical processes and kinetic reactions, that lead to partitioning of these heavy metal species into the fly ashes, as well as their emissions into the atmosphere.

## 2. Calculation methodology

### 2.1. Equilibrium calculation: method of element potentials

Equilibrium analysis of the incineration reaction system have been carried out by the method of element potentials [5] combined with atom population constraints to minimize the Gibbs energy of the reaction system. Each species has a chemical potential, defined as the amount of free energy contained per mol of that species, under the temperature, pressure and chemical composition of the incineration reaction system. The chemical potential is a function of temperature, pressure and number of moles of the species and is given for species  $i$  as:

$$\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{n_i \neq n_j, T, P = \text{constant}} \quad (2)$$

where  $\mu_i$  is the chemical potential of species  $i$ ,  $G$  is the Gibb’s free energy,  $n_i$  is the number of moles of species  $i$ , and  $T$  and  $P$  are temperature and pressure, respectively.

The total system Gibb's free energy can be found by summing all the individual chemical potentials, as follows:

$$G = \sum G_i = \sum n_i \mu_i \quad (3)$$

When a given mixture of species undergoes a change that minimizes the total Gibb's free energy, that change represents an equilibrium state, and corresponds to the complete conversion of reactants to products.

The method of element potentials treats the phases of a species as either ideal gases or ideal solutions and the Gibb's free energy is given by:

$$G_j = \sum \{ [G_i + \ln X_i] M_i \} \quad (4)$$

where  $X_i$  is the phase molar fraction of species  $i$ , and  $M_i$  is the moles of species  $i$ . The atom constraints are given by:

$$\sum \{ N_{i,j} M_i \} = A_j \quad (5)$$

where  $A_j$  is the moles of  $j$  atoms present and  $N_{i,j}$  is the number of  $j$  atoms in a molecule of species  $i$ . Using Lagrange multipliers ( $L_j$ ), one finds that:

$$X_i = \exp \{ -G_j + \sum [L_j N_{i,j}] \} \quad (6)$$

These Lagrange multipliers are the key to the method of element potentials. Since the element potential method is based on the free energy of atoms, the equilibrium state of these atoms (or minimized Gibb's free energy state) is independent of any reaction mechanism that changes the atoms from the initial (reactant) state to the final (product) state.

The computer code STANJAN [5] was used to perform the equilibrium calculations, at a range of temperatures expected in the operation of an actual municipal solid waste incinerator. Thermodynamic data for the species used in this study were obtained primarily from the JANAF tables [6] and compiled by Wu and Biswas [3].

## 2.2. Characterization of municipal solid wastes

Municipal solid waste is comprised of many different materials, including paper and cardboard boxes, plastics, yard trimmings, rubber, and a variety of inorganic materials. Ultimate analysis data [7] of a typical composition of MSW in the US was used to determine the primary constituents of the municipal solid waste feed, as given in Table 1. The total municipal solid waste feed consists of about 50% combustible material, 25% moisture and 25% inert (non-combustible) material. The combustible fraction contains some chlorine, sulfur and nitrogen (less than 0.5% each), with the bulk of the weight percentage as carbon, hydrogen and oxygen. This typical composition translates into a hydrocarbon fuel approximately represented by  $C_5H_8O_3$ . In addition, six trace metals (Al, Cd, Cr, Hg, Na, Pb) were included in the feed at average MSW levels, as determined by a Bureau of Mines study [8] and tabulated in Table 2. Most of the aluminum is found in the MSW as a non-combustible constituent, and only a small amount, 5400–12 000 ppm (see Table 2), is included in the combustible portion [8]. This composition is a typical MSW composition observed for the US and is not meant to

Table 1  
Typical ultimate analysis data for municipal solid wastes[7]

Analytical parameter	Wt%
Carbon	25.6
Hydrogen	3.4
Oxygen	20.3
Nitrogen	0.5
Chlorine	0.45
Sulfur	0.15
Moisture (H <sub>2</sub> O)	25.2
Ash (inert)	24.4
Higher heating value (cal g <sup>-1</sup> )	2472

represent the wide range of MSW compositions encountered over time and in different countries (for example, Germany has significantly less paper and more plastics, and the yard waste fraction in the US continues to decline [7]). The enthalpy of the combustible portion of the MSW was derived from the higher heating value (HHV) given in Table 1. The feed rate used in this analysis was 360 metric tons day<sup>-1</sup>, and was used as a base case by Wu et al. [2]. Typical feed rates vary from 135–400 ton day<sup>-1</sup> for rocking grate, continuous-flow stoker furnaces [8].

The metal species included in this thermodynamic analysis are given in Table 3. In addition to these species, the normal products of combustion (CO, H, OH, CO<sub>2</sub>, H<sub>2</sub>O) were included, as well as several chlorine species including free chlorine (Cl, Cl<sub>2</sub>, ClO, HOCl, HCl).

### 2.3. Estimation of incineration emissions

Calculations of the distribution of heavy metals between bottom ash, fly ash and flue gas were made to estimate the effect of solid waste composition variations on incineration emissions. First the STANJAN equilibrium calculations were used to estimate the split between bottom ash (solid) and vaporized (gaseous) metal compounds under combustion conditions. The gaseous compounds were then assumed to have exited the combustor and passed through a series of post-combustion zones (afterburner, heat transfer zone, electrostatic precipitator (ESP)) of varying temperatures, given in Table 4.

Table 2  
Metals in the combustible fraction of the municipal solid waste[8]

Element	Concentration average (ppm)	Concentration range (ppm)
Al	9000	5400–12000
Cd	9	2–22
Cr	55	20–100
Hg	1.2	0.66–1.9
Na	4500	1800–7400
Pb	330	110–1500

Table 3  
Metal species included in the equilibrium analysis

Pb[6]	Hg[6]	Cd[17]	Cr[6]	Na[6]	Al[6]
Pb(s)	Hg(g) Hg(l)	Cd(s) Cd(g) [18]	Cr(s)	Na(s)	Al(s)
PbCl(g) PbCl <sub>2</sub> (g)	HgCl(g) HgCl <sub>2</sub> (g)	CdCl <sub>2</sub> (l)	CrCl <sub>2</sub> (s) [17] CrCl <sub>3</sub> (s) [17] CrO <sub>2</sub> Cl <sub>2</sub> (g) [17]	NaCl(g) NaCl(l) NaCl(s)  Na <sub>2</sub> Cl <sub>2</sub> (g)	
PbO(g) PbO(l)	HgO(g)	CdO(s)	CrO <sub>2</sub> (g) CrO <sub>3</sub> (g) Cr <sub>2</sub> O <sub>3</sub> (s) CrO <sub>2</sub> OH(g) [19] CrO <sub>2</sub> (OH) <sub>2</sub> (g) [19] CrO(OH) <sub>3</sub> (g) [19] CrO(OH) <sub>2</sub> (g) [19]	NaOH(g) NaOH(l)	Al <sub>2</sub> O <sub>3</sub> (a)
PbSO <sub>4</sub> (s)			Na <sub>2</sub> CrO <sub>4</sub> (l)	NaAlO <sub>2</sub> (s) Na <sub>2</sub> CrO <sub>4</sub> (l) Na <sub>2</sub> SO <sub>4</sub> (l) Na <sub>2</sub> SO <sub>4</sub> (3)	NaAlO <sub>2</sub> (s)

Other species used: CO, CO<sub>2</sub>, H<sub>2</sub>O(g), H<sub>2</sub>O(l), OH, H, O, NO<sub>2</sub>, NO, Cl, ClOH, ClO, Cl<sub>2</sub>, HCl, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub> and S(l)

Rapid cooling in the post-combustion zones is assumed to freeze the chemical reactions. This frozen speciation is then used to establish at what location in the post-combustion zones saturation conditions are obtained for the different species. The post-combustion temperature history is used to predict when, and if, saturation would be reached. Saturation conditions occur when the saturation ratio ( $S$ ) exceeds 1.0:

$$S = \frac{P_{\text{vap}}}{P_{\text{sat}}} > 1.0 \quad (7)$$

where  $P_{\text{vap}}$  is the vapor pressure and  $P_{\text{sat}}$  is the saturation vapor pressure of a given species. When saturation conditions are reached for a given species, that species is assumed to completely condense on pre-existing seed particles. This particle size

Table 4  
Temperatures in the incinerator post-combustion zone

Distance (m)	$T$ (K)
0	Combustor Temp
10	600
14	500
15	400
22	333

Table 5  
Comparison of the time scales for nucleation and condensation for heavy metal species

Species	$\tau_N$ (s)	$\tau_C$ (s)
PbO	3.69	9.4e–10
PbCl	3.70	1.29e–6
PbCl <sub>2</sub>	4.52	3.66e–5
Hg	n/a	n/a
Cd	1.72	2.18e–3
HgCl	13.73	5.74e–3
HgCl <sub>2</sub>	13.73	6.15e–3

distribution of the seed particles is assumed to be representative of fly ash from a fluidized bed coal combustion system [9]. While generally, nucleation will compete with condensation to deplete the vapor cloud of a heavy metal species, the time scale for nucleation is much slower than for condensation for most species examined (PbO(g), PbCl(g), PbCl<sub>2</sub>(g), Hg(g), HgCl(g), HgCl<sub>2</sub>(g), Cd(g)) [10]. A comparison of nucleation time scales vs. condensation time scales is given in Table 5 and is based on the work of Wu and Biswas [10]. The condensation times are much shorter than the nucleation times for these species, especially in the presence of the typical seed particles. For estimation purposes, nucleation has been assumed to be negligible (note that times are not given for Hg, as it does not reach the saturation state). Using the particle size distribution of Carpenter et al. [9], the distribution of condensing species among the different particle sizes was found by calculating the flux of vapor molecules to the particle surface. At vapor saturation conditions, where the rate is governed by random molecular collisions, the flux of molecules to the surface ( $n_z$ ) is calculated by the following equation [11]:

$$n_z = \frac{2\pi D d_p}{kT} (P_{\text{vap}} - P_d F(Kn)) \quad (8)$$

where  $d_p$  is the diameter of the particle,  $p_d$  is the partial pressure of the vapor at the surface of the particle,  $D$  is the diffusivity of the vapor,  $T$  is the temperature,  $Kn$  is the Knudsen number, and  $k$  is Boltzmann's constant. Eq. (8) is valid for all regimes (continuum, transition and non-continuum) with  $F(Kn)$  as a correction factor for the transition and non-continuum regimes.  $F(Kn)$  is determined as follows:

$$F(Kn) = \frac{1 + Kn}{1 + 1.71 Kn + 1.333 Kn^2} \quad (9)$$

The partial pressure of the vapor at the surface of the particle ( $p_d$ ) is assumed to be zero due to the very low concentrations of the metal species in the free gas stream. The flux to the particles of different sizes can be used to determine what size fraction will contain the majority of the metals, either in the fly ash, or more importantly, in the exhaust flue gas.

Finally, using estimates of ESP (electrostatic precipitator) efficiency [12], given as a function of particle size, an estimate is made of how much of each species is captured as fly ash, and how much escapes capture by the ESP. These two estimates are listed as 'fly ash' and 'flue gas', respectively, in the results.

### 3. Discussion of results

Two separate calculations were carried out in this study. First, baseline calculations were made to determine the impact of variation of waste moisture content on heavy metal emissions with average sodium and chlorine waste composition data. Then a second calculation was made, varying the sodium feed content to determine how variation in sodium content would affect the heavy metal speciations and emissions. Table 6 shows the conditions under which these calculations were made and Table 7 shows a comparison of the results from these runs. Both sodium and waste moisture values are expected to vary locally and over time, and the concentration values for sodium variation were taken from studies of typical MSW composition in the US [8].

#### 3.1. Baseline calculation

Normal waste moisture content is 25.2 wt%. This is the typical value for the US, UK and the Netherlands, with Germany, France, and Switzerland averaging closer to 35% [7]. The effects of variation in waste moisture can be examined for two different possible operational modes of the incinerator: (1) variation in moisture at a constant incineration temperature, simulating an incinerator controlled to a specific temperature by varying the excess air, and (2) variation in moisture resulting in a change in incineration temperature, simulating an incinerator where temperature is not controlled above a certain minimum value ('flameout'), and is allowed to vary with incoming moisture content (holding excess air constant). Under normal operation of most municipal incinerators, Mode 1 operation is the most commonly used.

In this study, the waste moisture content was varied from 0% to 37% by weight at constant temperature. The baseline calculation was also conducted over a range of temperatures representing the expected variation in operating temperature (1123–1323 K) with the variation in waste moisture, thus simulating both modes of operation (note that the constant air calculations were performed over the range of 8–37% moisture corresponding to the temperature range 1323–1123 K). Average values of all trace metals (including lead and sodium) were assumed. Table 6 illustrates the range of temperatures and waste moisture used in this study.

Table 6  
List of simulations performed

<i>T</i> (K)	1123, 1173, 1223 (typical), 1273, 1323
Waste moisture (%)	0.0, 2.9, 8.1, 15.0, 20.9, 25.2 (typical), 29.1, 32.0, 34.6, 37.0
<i>Runs</i>	
Case 1	Baseline (All metals held constant at average concentrations, see Table 2)
Case 2	Sodium (All metals held constant at average concentrations, except sodium which is held at a higher concentration (6560 ppm))

Each case was run at five different temperatures and each temperature with 10 different waste moistures. The total runs for each case was 50 runs. Each run held all MSW constituents constant (as listed in Table 1) except those explicitly mentioned above.



Table 7  
Results of equilibrium calculations at constant temperature<sup>a</sup>

T = 1223 K (Mode 1)										
Run	H <sub>2</sub> O	Cl	HCl	NaCl(g)	PbO(l)	PbCl <sub>2</sub> (g)	PbO(g)	Pb% in gas	% in fly ash	% in bottom ash
Baseline	0%	1.85e-3	4.13e-1	1.00e-1	1.37e-3	3.46e-3	1.03e-4	2.8%	69.4%	27.8%
	25%	1.44e-3	4.31e-1	9.17e-2	1.91e-3	2.86e-3	1.51e-4	2.4%	59.0%	38.6%
	37%	1.28e-3	4.38e-1	8.84e-2	2.19e-3	2.54e-3	1.80e-4	2.1%	53.6%	44.3%
High sodium (6560 ppm)	0%	1.09e-3	2.43e-1	2.05e-1	2.62e-3	2.14e-3	1.85e-4	1.8%	45.8%	52.3%
	25%	8.63e-4	2.58e-1	2.00e-1	3.14e-3	1.58e-3	2.33e-4	1.4%	36.0%	62.6%
	37%	7.75e-4	2.66e-1	1.98e-1	3.36e-3	1.34e-3	2.58e-4	1.3%	31.8%	66.9%

T = 1323 K (Mode 1)										
Run	H <sub>2</sub> O	Cl	HCl	NaCl(g)	PbO(l)	PbCl <sub>2</sub> (g)	PbO(g)			
Baseline	0%	2.57e-3	2.83e-1	2.55e-1	2.08e-3	1.69e-3	1.02e-3			
	25%	2.09e-3	3.09e-1	2.35e-1	2.36e-3	1.23e-3	1.21e-3			
	37%	1.89e-3	3.20e-1	2.27e-1	2.47e-3	1.03e-3	1.31e-3			
High sodium (6560 ppm)	0%	1.69e-3	1.87e-1	3.39e-1	2.70e-3	8.94e-4	1.24e-3			
	25%	1.41e-3	2.08e-1	3.23e-1	2.84e-3	6.37e-4	1.37e-3			
	37%	1.29e-3	2.18e-1	3.16e-1	2.89e-3	5.31e-4	1.44e-3			

<sup>a</sup> All quantities are mol s<sup>-1</sup> unless indicated otherwise.

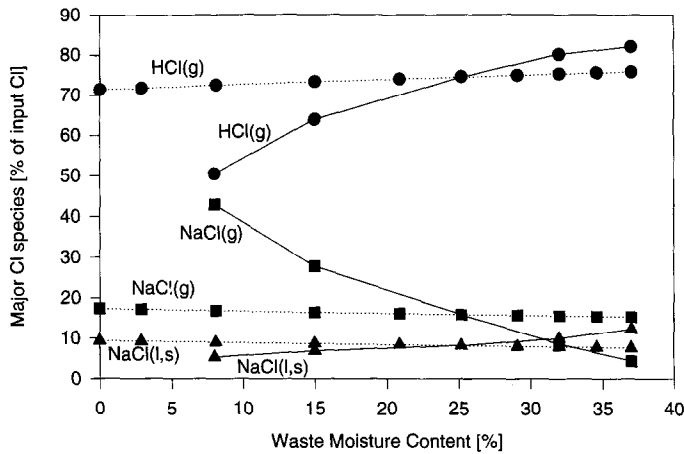


Fig. 1. Major chlorine species plotted as a function of waste moisture content at baseline conditions. (... Mode 1; — Mode 2; ●: HCl(g); ■: NaCl(g); ▲: NaCl(l, s)).

### 3.2. Effects of waste moisture on heavy metal speciations

The effect on heavy metal speciation of changing waste moisture versus changing temperature is significant. Mode 1 (constant temperature) separates these two effects, while Mode 2 (constant excess air) combines them. The results (Figs. 1 and 2) indicate that most of the chlorine in the reaction mixture is bound with hydrogen (HCl) and gaseous sodium (NaCl) at all moisture and temperature levels. Fig. 1 shows the major chlorine species (NaCl and HCl) as a function of the waste moisture at constant temperature (Mode 1-1223 K) and for varying temperature (Mode 2 constant air).

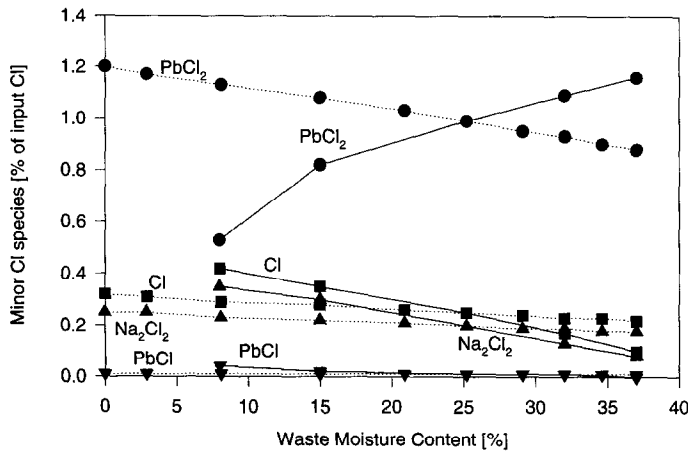


Fig. 2. Minor chlorine species plotted as a function of waste moisture content at baseline conditions. (... Mode 1; — Mode 2; ●: PbCl<sub>2</sub>; ■: Cl; ▲: Na<sub>2</sub>Cl<sub>2</sub>(g); ▼: PbCl).

HCl(g) is the dominant species over the entire temperature range and waste moisture content range, which agrees with previous equilibrium calculations [3,14]. The amount of HCl increases with increasing waste moisture, as the water provides more hydrogen to combine with chlorine. Fig. 1 illustrates how the HCl–NaCl split is fairly constant, as a function of waste moisture, for Mode 1 (constant temperature) operation, but varies considerably for Mode 2 (constant air) operation. This implies that temperature is a larger controlling factor than moisture content, and shifts in the HCl–NaCl equilibrium towards more NaCl with increasing temperature. The free chlorine is a small (< 0.5%) fraction of the total chlorine loading, as shown in Fig. 2. As moisture is increased from 0 to 37 wt%, free chlorine decreases by approximately 30% in Mode 1 (from 0.32% to 0.22% of total chlorine), as a result of the formation of more HCl from excess hydrogen provided by the increased waste moisture. In Mode 2 (constant airflow), as moisture content is increased, free chlorine decreases approximately 75%, due to the additional effect of decreasing temperature shifting the equilibrium to favor HCl formation. This reduction in free chlorine also has implications for the potential to form lower amounts of chlorinated organics, as well as metallic chloride species.

Waste moisture content also has a significant effect on the lead speciation. Fig. 3 shows how speciation between  $\text{PbCl}_2$  and  $\text{PbO}$  changes with moisture content. Under Mode 1 operation at 1223 K, increases in waste moisture content shift the lead from the gaseous  $\text{PbCl}_2(\text{g})$  to the solid  $\text{PbO}(\text{l})$ , due to the reduction in available chlorine to combine with the lead. The variation of the speciation with moisture is even greater at lower temperatures. Under Mode 2 operation, where the temperature is allowed to vary, increases in moisture content (resulting in a decrease in temperature) shifts the lead from the oxide form  $\text{PbO}(\text{l})$  to the gaseous chloride form  $\text{PbCl}_2(\text{g})$ . This demonstrates, similar to the HCl–NaCl equilibrium, that temperature is the larger controlling factor.

Additional calculations, not shown, were performed to include the  $\text{PbCl}_4$  species in the equilibrium calculations. This species is favored under equilibrium conditions and

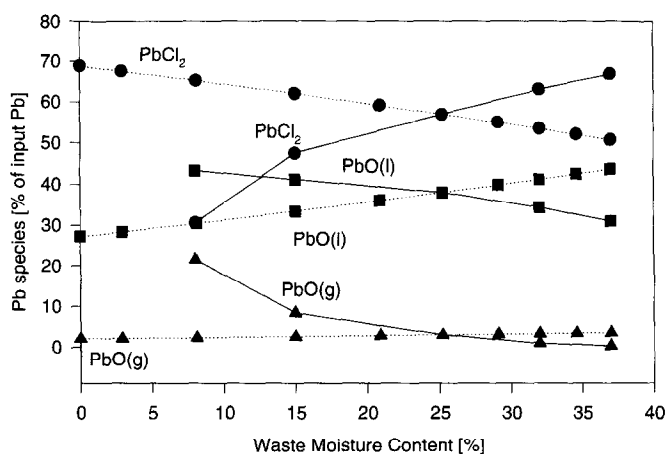


Fig. 3. Lead speciation as a function of waste moisture content at baseline conditions. (...Mode 1; — Mode 2; ●:  $\text{PbCl}_2$ ; ■:  $\text{PbO}(\text{l})$ ; ▲:  $\text{PbO}(\text{g})$ ).

this was reflected in the calculations.  $\text{PbCl}_4$  was the dominant lead species at all temperatures and waste moisture contents. However,  $\text{PbCl}_4$  is not observed generally in the field (it decomposes at  $105^\circ\text{C}$  and therefore cannot exist at high temperatures) and is known to be limited kinetically [3]. Therefore  $\text{PbCl}_4$  was not included in this analysis.

Mercury and cadmium have virtually no oxide or chloride speciation, with the primary constituent being the gaseous elemental form at all temperatures and moisture levels (approximately 2% of the mercury is in the  $\text{HgO}(\text{g})$  form). Chromium is mostly bound with oxygen, with approximately 60%  $\text{Cr}_2\text{O}_3(\text{s})$  and 37%  $\text{Na}_2\text{CrO}_4(\text{l})$ . This speciation varies significantly with temperature (Mode 2) and increases in waste moisture tend to increase the percentage that is bound with sodium. The chromium chloride species are very small, even compared to free chlorine levels.

In summary, in Mode 1 (constant temperature) operation, an increase in waste moisture content from 0% to 37% increases the amount of HCl, decreases the amount of free chlorine up to 30%, shifts lead from the chloride to oxide forms, but has little effect on the chromium, mercury and cadmium speciation. If, however, the temperature is allowed to vary with increases in waste moisture content (Mode 2, constant airflow), then increases in waste moisture content from 0% to 37% will still increase the amount of HCl, decrease the amount of free chlorine up to 75%, and will shift the lead from the solid oxide to the gaseous chloride form.

### 3.3. Effects of waste moisture on heavy metal emissions from incinerators

The above equilibrium calculation results are conducted at combustion temperatures and represent the equilibrium condition in the combustor at the given waste moisture and incineration temperature. Translating these speciation estimates to emissions values is difficult at best. Due to complex aerosol nucleation, vapor condensation and kinetic (non-equilibrium) reactions, modeling the emissions characteristics in the post-combustion zone is quite involved [13]. However, by making some simplifying assumptions similar to those made by Wu and Biswas [3] and Wu et. al. [4], some comparisons to field data can be made. Assuming that all solid phase products in the combustor become part of the bottom ash, then only gaseous products would exit the combustion zone. Assuming, as well, that no further chemistry occurs (due to rapid cooling in the post-combustion zone), and that all gaseous products will condense upon reaching saturation conditions, estimates can be made on the amount of metal compounds distributed among the fly ash seed particles. In reality, some of the gaseous products will nucleate, rather than condense, and some will stay in the gas phase (complete depletion of the vapor cloud will not occur). However, if we make these assumptions, an estimate can be made for the distribution of metallic species amongst the bottom ash, fly ash, and flue gas.

Fig. 4 shows the variation of fly and bottom ash with waste moisture for both Mode 1 and Mode 2 operation. Calculation of the split between bottom ash, fly ash and flue gas emissions were made using Eqs. (6)–(8) in addition to the chemical equilibrium calculations. As shown in Fig. 4, the flue gas exhaust accounts for only a small portion of the total lead in both modes of incinerator operations. This is assuming that the ESP operates under optimal conditions. The emission may be larger under non-optimal

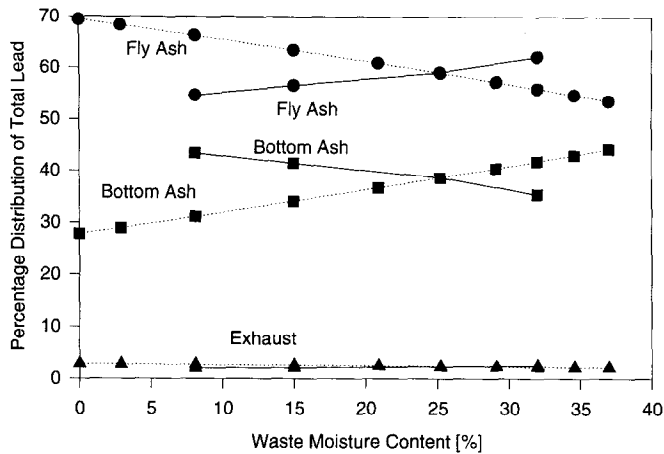


Fig. 4. Lead emissions as a function of waste moisture content at baseline conditions. (...Mode 1; — Mode 2; ●: Fly ash; ■: Bottom ash; ▲: exhaust).

operating conditions for the ESP. Fig. 4 also shows the split of lead in between the bottom ash and fly ash. In Mode 1 operation (constant temperature), which is most commonly used in most municipal incinerators, more total lead is shifted from the fly ash to the bottom ash as the waste moisture is increased. The fly ash fraction decreases from approximately 68% to 54% when the waste moisture content is increased from 5% to 37%. This is similar to the finding of a previous study by Verhulst et al. [14] on the speciation of Zn in municipal solid waste incineration systems. This modest change in the percentage of lead in fly ash is largely due to the decrease in the amount of lead species in the gas phase as a result of the shift from  $\text{PbCl}_2(\text{g})$  to  $\text{PbO}(\text{l})$  with increases in moisture content. Increases in waste moisture result in more of the chlorine being associated with hydrogen relative to lead, essentially reducing the  $\text{PbCl}_2(\text{g})$  vapor cloud available for condensation onto fly ash in the post-combustion zones. This, in turn, results in less lead in the fly ash and more lead in the bottom ash. In Mode 2 operation (varying temperature, constant airflow), there is an increase in the total lead found in the fly ash fraction with increasing moisture. This is due to the increase in total lead in the gas phase, which is due to the equilibrium shift from  $\text{PbO}(\text{l})$  to  $\text{PbCl}_2(\text{g})$  with the decrease in temperature accompanying the increase in moisture for Mode 2. This is only true for average sodium levels, as will be discussed later.

Similar estimates for cadmium and mercury show that 98.1% of the cadmium is captured in the ESP before exiting the stack, but that 100% of the mercury remains in the gaseous phase (does not reach saturation conditions before exiting the stack) and thus is not captured. Waste moisture content and temperature have little impact on these results, because the variation in waste moisture does not affect the speciation in the combustor.

As discussed earlier, in order to translate the heavy metal speciation data in the combustion mixture to emission data in terms of bottom ash, fly ash and exhaust, simplifying assumptions similar to those used by Wu and Biswas [3] and Wu et al. [4]

had to be used. To assess the validity of these assumptions, the estimates from this study are compared to previous measurements in the Bamberg incineration plant by Reimann [15], which reported the split between bottom ash and the raw gas (fly ash and stack exhaust) for several heavy metals. The measurements by Reimann [15] gave 33% of the lead in the raw gas and 67% in the bottom ash. Our estimates in this work indicate that, at 4500 ppm of Na and 25% of waste moisture (baseline conditions), 61% of the lead is volatilized into the fly ash and flue gas exhaust (raw gas) and 39% is in the bottom ash. If the Na content is increased to 6560 ppm, 37% of the lead is estimated to be volatilized into the raw gas and 63% remain in the bottom ash. Although the waste moisture and sodium contents for the measurements by Reimann [15] are unknown, our model estimates are reasonably close to the measurements. Therefore, the assumptions made in this work for lead emission estimates are judged reasonable.

The reduction in the lead in fly ash is expected to reduce proportionately the overall atmospheric emissions of this heavy metal in many incineration plants that are not yet equipped with state-of-the-art flue gas cleaning technologies. In addition, the predicted changes in the lead speciation may also have significant implication on the flue gas cleaning efficiency for lead and the leachability of lead in the fly ashes when they are captured by flue gas cleaning for land disposal [16].

### 3.4. Effects of increased waste sodium on heavy metal speciations

As discussed earlier, increasing waste sodium content may have the effect of decreasing free chlorine and increasing the fraction of sodium-species, thus increasing the fraction of chlorine associated with NaCl. Fig. 5 shows that at nearly 1.5 times of the baseline sodium, content, i.e., at 6560 ppm, the fraction of the total chlorine in the form of NaCl increases when compared to baseline sodium levels (4500 ppm), under Mode 1 conditions. While NaCl levels increase at the higher sodium concentration, HCl is still

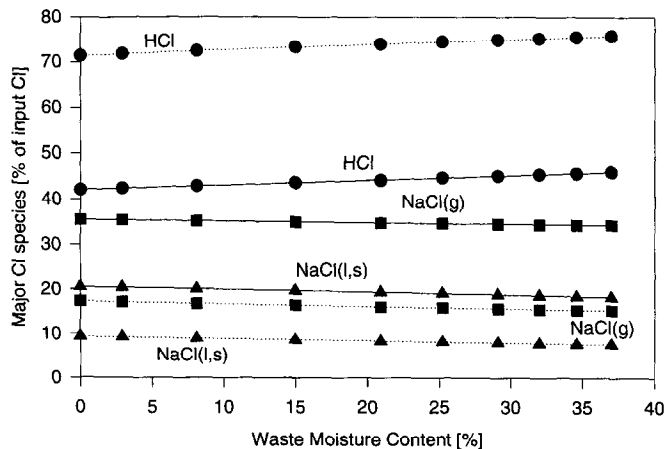


Fig. 5. Major chlorine speciation as a function of waste moisture content for Mode 1. (—: Max sodium vs baseline... avg sodium) (●: HCl(g); ■: NaCl(g); ▲: NaCl(l, s)).

the dominant species for the entire range of waste moisture content and temperature. In addition, the condensed phase NaCl species (liquid and solid) account for a significant fraction of the total chlorine in the system at the lower temperatures. Free chlorine is approximately 40% less for the high sodium case (as compared to average sodium levels, see Table 7), and there is significantly less variation of free chlorine with waste moisture. It appears that the sodium is able to remove some of the free chlorine from the system, thus reducing the effect that additional hydrogen (from excess waste moisture) has on reducing free chlorine. Not only the overall free chlorine level is reduced when sodium is increased, but there is also a reduction in the other minor chlorine species,  $\text{PbCl}_2$  and  $\text{PbCl}$ , as shown for  $\text{PbCl}_2$  in Fig. 6. Overall, increasing sodium levels appears to lessen the impact of waste moisture on heavy metals speciation.

Lead speciation is affected mainly by a shift from  $\text{PbCl}_2(\text{g})$  to  $\text{PbO}(\text{l})$  with an increase in waste sodium content. Since the excess sodium combines with chlorine, reducing minor chlorine species (including  $\text{Cl}$  and  $\text{PbCl}_2$ , as seen in Table 7),  $\text{PbCl}_2$  becomes a smaller fraction of the total lead. While the amount of  $\text{PbO}$  in the gaseous phase remains largely dependent on temperature (it is constant with respect to moisture),  $\text{PbO}$  in the liquid phase makes up the remainder of the lead not combined with chlorine, and increases for the high sodium case. In Mode 1, the absolute levels of  $\text{PbO}(\text{l})$  and  $\text{PbCl}_2$  are different between the average and high sodium cases, but the trends with increasing waste moisture are nearly the same, as seen in Fig. 6, i.e., decreasing total lead in the gas phase combustion mixture ( $\text{PbCl}_2(\text{g}) + \text{PbO}(\text{g})$ ) with increasing moisture. In Mode 2, the absolute levels of  $\text{PbO}(\text{l})$  and  $\text{PbCl}_2(\text{g})$  between average and high sodium are also different (see Table 8). However, the trends with increasing moisture are different for differing sodium levels. For the average sodium levels, the total lead in the gas phase actually slightly increases with increasing moisture. For the maximum sodium levels, the total lead in the gas phase decreases with increasing moisture. This illustrates

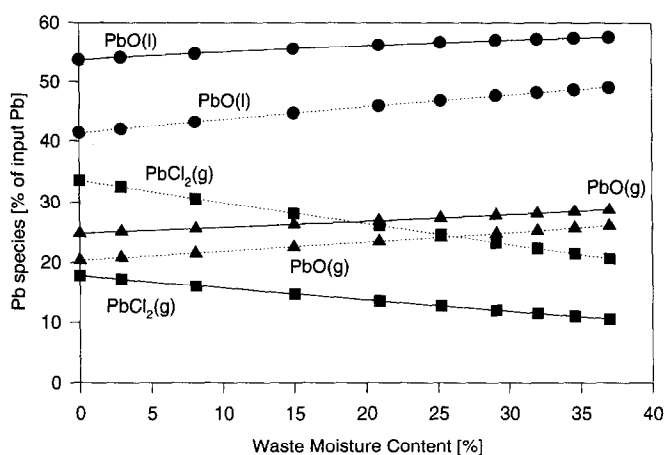


Fig. 6. Lead speciation as a function of waste moisture content for Mode 1 (— Max sodium vs baseline ... avg sodium) (●:  $\text{PbO}(\text{l})$ ; ■:  $\text{PbCl}_2$ ; ▲:  $\text{PbO}(\text{g})$ ).

Table 8  
Results of equilibrium calculations at constant combustion airflow (Mode 2)<sup>a</sup>

Run	H <sub>2</sub> O	Cl	HCl	NaCl(g)	PbO(l)	PbCl <sub>2</sub> (g)	PbO(g)
Baseline	8% (1323 K)	2.40e-3	2.92e-1	2.48e-1	2.17e-3	1.54e-3	1.08e-3
	25% (1223 K)	1.44e-3	4.31e-1	9.17e-2	1.91e-3	2.86e-3	1.51e-4
	37% (1123 K)	6.03e-4	4.74e-1	2.51e-2	1.56e-3	3.36e-3	1.43e-5
High sodium (6560 ppm)	8% (1323 K)	1.60e-3	1.94e-1	3.33e-1	2.75e-3	8.06e-4	1.28e-3
	25% (1223 K)	8.63e-4	2.58e-1	2.00e-1	3.14e-3	1.58e-3	2.33e-4
	37% (1123 K)	3.22e-4	2.54e-1	7.62e-2	3.21e-3	1.77e-3	2.64e-5

<sup>a</sup>All quantities are mol s<sup>-1</sup> unless indicated otherwise.

the dominant effect of temperature on the speciation of the lead, favoring PbCl<sub>2</sub>(g) over PbO(l) as temperature decreases. In the case of high sodium, the equilibrium is pushed towards PbO(l) because of the scavenging of Cl by the excess sodium, so much so that even at reduced temperatures, PbO(l) is still more favored than PbCl<sub>2</sub>(g).

Chromium speciation is affected by the increase in sodium levels primarily by increasing the proportion of chromium bound with sodium, Na<sub>2</sub>CrO<sub>4</sub>(l). This reduces the amount of Cr<sub>2</sub>O<sub>3</sub> and also decreases the variation with temperature and waste moisture levels. This also indicates that as sodium levels increase, chromium is changing form, from trivalent (Cr<sub>2</sub>O<sub>3</sub>) to the more toxic hexavalent (Na<sub>2</sub>CrO<sub>4</sub>). Mercury and cadmium remain primarily in their elemental gaseous forms, with negligible oxide or chloride speciation.

### 3.5. Effects of increased waste sodium on heavy metal emissions

Under normal operation of municipal incinerators (Mode 1), increased sodium content in the waste impacts the lead emissions in two different ways. First, increased sodium content reduces significantly the percentage of lead in the fly ash and increases the lead percentage in the bottom ash. As shown in Fig. 7, at the normal moisture level of the waste (25%), the percentage of lead in the fly ash decreased from 59% to 36% when the sodium content increases from the average of 4500 ppm to the upper limit of 6560 ppm. This trend is generally true at all waste moisture levels.

Second, at the higher sodium content in the waste feed, the impact of waste moisture on the lead speciation in the fly ash is slightly reduced. This is because an increase in the waste sodium content increases the competition for free chlorine in the combustion system, resulting in less formation of lead chloride species. As shown in Fig. 7, at sodium content of 6560 ppm, the percentage of lead in the fly ash decreases from about 43% to about 32% when the waste moisture content is increased from 5 to 37%. This decrease in fly ash lead is just slightly less than that at the normal sodium content of 4500 ppm in the waste feed.

As shown in Figs. 4 and 7, a reduction in waste moisture content in the incineration feed results in a modest shift in the percentage of lead in the PbO species to PbCl<sub>2</sub> in the incineration reaction mixture, which lead to a shift of the lead metal from the bottom



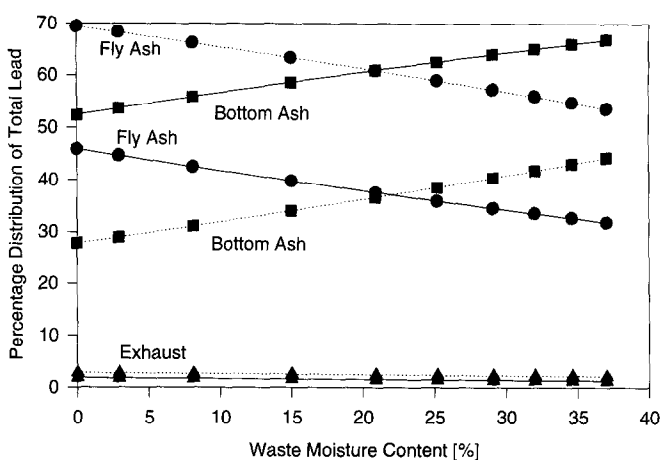


Fig. 7. Lead emissions as a function of waste moisture content Mode 1. (— Max sodium vs baseline... avg sodium). (●: Fly ash; ■: bottom ash; ▲: exhaust).

ash to the fly ash in the incineration plant. Changes in the waste sodium content has a similar effect on the lead speciation, although these effects are more pronounced than waste moisture. Also shown in the two figures are calculated lead emissions in the incineration stack exhaust, based on a model for the electrostatic precipitator. The variations in waste moisture and sodium content are estimated to have fairly small impact on the incineration stack emissions of lead. Nevertheless, under realistic incineration conditions, a portion of the lead in the incineration waste feed is emitted in the stack exhaust with the small fly ash particles. Therefore, the increase in the lead in fly ash caused by the reduction in the waste moisture and sodium content can lead to a proportionate increase in the overall atmospheric emissions of lead, especially for those incineration plants that are not equipped with extensive state-of-the-art flue gas cleaning technologies. In addition, the predicted shifts in the lead speciation may also have significant implications to the flue gas cleaning efficiency for lead, as well as the leachability of lead in the fly ashes when they are captured by flue gas cleaning for land disposal. More studies are needed before these impacts can be addressed in detail.

#### 4. Conclusions

By examining the effects of waste moisture and sodium content levels on chlorine and heavy metals speciation in incinerator combustion systems, equilibrium trends and emissions estimates predict the following.

(1) Free chlorine is reduced with increases in waste moisture and sodium contents in MSW feed.

(2) Lead is preferentially in the gaseous oxide form at high temperatures and the gaseous chloride form at low temperatures in the combustion mixture. Increases in

sodium levels deplete the free chlorine and reduce the chloride form of lead, working in opposition to the equilibrium temperature effects. Increases in waste moisture, at constant temperature, shifts the speciation of lead from the chloride to the oxide form, thus reducing the percentage of the lead in fly ash. Increases in temperature shift the lead speciation equilibrium towards the liquid lead species (PbO(l)). Therefore, increases in waste moisture, increases in temperature and increases in sodium levels all independently reduce the amount of lead in the fly ash. At average sodium levels, decreases in temperature with increases in waste moisture (via Mode 2 operation) increases the amount of lead in the fly ash. These shifts in the lead speciation in the incineration system are not expected to impact significantly the stack emissions of lead, based on the use of an effective electrostatic precipitator. Nevertheless, under realistic incinerator operating conditions, the increase in the lead in fly ash may be expected to lead to a proportionate increase in the overall atmospheric emissions of lead, especially for those incineration plants that are not equipped with state-of-the-art particle and flue gas cleaning technologies. In addition, the predicted changes in the lead may also have significant implication on the flue gas cleaning efficiency for lead and the leachability of lead in the fly ashes when they are captured by flue gas cleaning for land disposal.

(3) Cadmium and mercury are preferentially in the elemental gaseous form, with the oxide and chloride forms being negligible at all waste moisture contents, and sodium contents examined. Mercury remains in the gaseous form even at exit (exhaust) temperatures, and is unaffected by the waste moisture or sodium levels. Cadmium reaches saturation conditions in the post-combustion zone and is expected to condense entirely onto fly ash. Most of this fly ash is captured. Cadmium emissions are also unaffected by the waste moisture or sodium levels.

(4) Chromium has a higher tendency to combine with sodium ( $\text{Na}_2\text{CrO}_4$ ), and increases in sodium input levels increase  $\text{Na}_2\text{CrO}_4$  levels substantially. Remaining chromium is in the oxide form, and there is negligible chromium chloride at all temperatures and waste moisture levels examined. Since all forms of chromium are in the liquid or solid form, changes in waste moisture are not expected to affect the ash–gas emissions split.

Overall, the above equilibrium study is useful in determining the preferential state of metal species as a function of waste moisture and sodium levels. The results indicate that, at the typical municipal incineration temperature of  $950^\circ\text{C}$ , a decrease in the waste moisture content from 37% to 5% results in a modest increase in the percentage of the lead in the fly ash from about 54% to 68% of the total. Since waste moisture is one of the most variable factors in MSW content, and 5% is a relatively small waste moisture content, the impact of variation in waste moisture on lead in the fly ash would appear to be rather small. However, a decrease in the waste sodium content from 6560 ppm (upper limit for MSW content) to 4500 ppm (MSW average) results in a more significant increase in the percentage of lead in the fly ash from 36% to 60% at the average waste moisture content. Several other heavy metals have also been studied, but the impacts are much smaller. Estimates of incineration emissions were made using highly simplified expressions of the complex aerosol formation processes that occur in the post-combustion zones. The estimates for lead are roughly consistent with measurements in the municipal incineration plants.

## 5. Nomenclature

### 5.1. English

$A_j$	Moles of $j$ atoms present.
$d_p$	Diameter of the particle.
$D$	Diffusivity of the vapor.
$G$	Gibb's free energy.
$G_i$	Gibb's free energy of species $i$ .
$G_j$	Gibb's free energy of atom $j$ .
$k$	Boltzmann's constant = $1.38 \times 10^{-23}$ J molecule <sup>-1</sup> K <sup>-1</sup> .
$Kn$	Knudsen number = $\frac{2\lambda}{d_p}$
$L_j$	Element potential for $j$ atoms (Lagrange multiplier).
$M_i$	Moles of species $i$ .
$n_i$	Number of moles of species $i$ .
$N_{i,j}$	Number of $j$ atoms in a molecule of species $i$ .
$n_z$	Flux of molecules to the surface.
$p_d$	Partial pressure of the vapor at the surface of the particle.
$P_{\text{sat}}$	Saturation vapor pressure of a given species.
$p_{\text{vap}}$	Vapor pressure of a given species.
$S$	Saturation ratio.
$T$	Temperature.
$X_i$	Phase mole fraction of species $i$ .

### 5.2. Greek

$\mu_i$	Chemical potential of species $i$
$\lambda$	Mean free path.

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