

On the Fate of Heavy Metals in Municipal Solid Waste Combustion Part II: From Furnace to Filter

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ABSTRACT

The chemistry and behaviour of the heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn as they move from the furnace to the filter in a combustion plant for MSW, has been investigated. Focus has been on the influence of varying MSW composition and operational parameters such as air/fuel ratio and temperature. It was found that only Hg is present in gas phase after the boiler at 500 K. The availability of sulphur and chlorine largely influenced the condensing behaviour and chemistry for many of the heavy metals. One important observation is the shift from solid phase chlorides to sulphates at temperatures below 900 K for Pb and Zn, when increasing the sulphur availability, Pb and Zn sulphates being less corrosive in boiler systems than their respective chlorides.

***Keywords:** MSW Combustion, heavy metals, equilibrium calculations*

1. INTRODUCTION

Heavy metals in waste entering a combustion plant may end up in the bottom ash, fly ash, flue gas cleaning residues or in the flue gas. Hence, all mass flows coming out of the combustion plant are potentially an environmental hazard. In addition to the environmental hazards [1] some heavy metals also constitute operational hazard due to corrosion. Krause [2] showed that certain heavy metal species such as lead and zinc chlorides are highly corrosive and therefore unwanted in the boiler system. In order to cope with both environmental and operational issues caused by heavy metals in waste combustion, more knowledge is needed. The partitioning of the different heavy metals and the chemistry of the heavy metals bound in the ashes determines the concentration and the potential of leachability when utilising the bottom or fly ash for other purposes than landfilling. Knowledge on the volatile and condensing behaviour of heavy metal species in a combustion plant is important in order to assess the emission potential of heavy metal species. Heavy metal species condensing on very small particles or aerosols, which typically are formed late in the cooling process of the flue gas, have a larger potential to escape through the stack as larger particles will be captured by the flue gas cleaning system [3]. A study performed by Ghorishi and Gullett [4] showed that the knowledge of the chemical form of mercury, when entering the flue gas cleaning system is important, in order to choose the right sorbent for removal of mercury. Hence, there are several reasons why knowledge on the partitioning and chemistry of heavy metal species in MSW combustion plants are needed. This work is a part of a more comprehensive work on the fate of heavy metals in MSW combustion. The overall objective of the work is to gain more knowledge on the partitioning and chemistry of heavy metals in MSW combustion. The first part of this work [5] is concerned with the devolatilisation of heavy metals on the grate, while this second part is concerned with the behaviour from furnace to filter.

Several studies using equilibrium calculation systems on the behaviour for heavy metals in combustion systems has been undertaken [6-10]. As opposed to the work mentioned above ash species have been included since they may interact chemically with heavy metals to form, for instance, silicates, aluminates and/or aluminosilicates and thereby influence the distribution and volatility of heavy metals in combustion of MSW. The including of ash species and lack of knowledge on the behaviour of heavy metals in MSW combustion systems has motivated this work. The objective of this study is therefore to investigate the influence of varying operational parameters and MSW compositions on the equilibrium chemistry and condensing behaviour at typical combustion conditions in a grate furnace. Focus is on the influence of temperature, Cl/metal- and S/metal ratios, fly ash content and fuel/air ratio.

2. EQUILIBRIUM CALCULATIONS

Included in this equilibrium study are eight heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, Zn and the ash species Aluminium (Al), Calcium (Ca), Iron (Fe) and Silicone (Si). A brief description of the equilibrium program (MINGTSYS) and its limitations and possibilities are described elsewhere [5, 11]. The chemistry and condensation behaviour of the different metals are in focus in this study. A comparison of *trends* observed from experimental investigations in literature with global equilibrium analysis (GEA) on condensation in the flue gas by performing a comprehensive parametric study is performed. In this part of the study, only oxidising conditions are applied since there always will be enough oxygen in this system if one does not take into account possible local conditions. The species used in the equilibrium calculations together with the assumptions used for determining the elemental composition are listed in the first part of this work [5]. The ultimate compositions of the waste together with the “base case” composition for equilibrium calculations are given in Table 1. In order to investigate how the distribution of heavy metals changes as a

function of temperature from the furnace to the filter (cooling of flue gas) calculations were performed under oxidising conditions under the assumption that 3 wt% of the total ash content followed the flue gas as fly ash through the boiler to the electrostatic precipitator (ESP) [12].

Calculations with a composition simulating Refuse Derived Fuel (RDF) were also performed in order to study the influence of differences in the elemental composition (C/H/O/N) and ash content. It was discovered that the ash content had a significant influence on the equilibrium distribution all heavy metals except Hg. The content of Cl, S and heavy metals were kept the same for MSW and RDF in these calculations for comparison purposes.

In MSW combustion there are two important factors controlling the fate of heavy metals; waste composition and operational parameters such as air supply and temperature profile through the combustion plant. A parametric study has therefore been performed in order to investigate the effect of these parameters at typical conditions for MSW grate combustion. The Cl/C_{BC} ratio denotes the actual number of moles of Cl used in the calculations to the number of moles at base case conditions. On an as received mass basis the chlorine and sulphur content of the waste is varied between 0.06-5.7wt% ($Cl/C_{BC} = 0.1-10$) and 0.02-1.7 wt% ($S/S_{BC} = 0.1-10$), respectively. The fly ash content is varied between 1-6 wt% ($Ash/Ash_{BC} = 0.3-2.0$) of the total ash concentration of the waste. The air/fuel ratio (λ) is varied between 1.1-1.9.

3. RESULTS AND DISCUSSION

An adiabatic flame temperature of ~ 1500 K was calculated using the base case fuel composition and $\lambda = 1.9$. In addition, Gort [13] showed that a maximum temperature of

~1600 K was obtained in the reaction front of MSW in a packed bed. Therefore a maximum temperature of 1600 K was chosen, while 300 K is chosen as the lower temperature in order to be on the low side of temperatures observed when entering the filter system (typically 500 K).

The temperature of the flue gas when it enters the flue gas cleaning system is important in order to evaluate the amount of condensed heavy metals. This temperature might vary, but in the following discussion a temperature in the range 300-500 K has been assumed. Due to the uncertainty on the fraction of heavy metals that will remain in the bottom ash, it has further been assumed that all metals are fully volatilised and found in the flue gas with the same amount as in the MSW. The equilibrium distribution of all heavy metals simulating the conditions from the furnace to the filter is shown in Figure 1. When interpreting the results it is important to know the equilibrium distribution of chlorine and sulphur, since these species will affect the distribution of the heavy metals. The equilibrium distributions for chlorine and sulphur at base case conditions are shown in Figure 3 in the Appendix. At high temperatures chlorine is mainly present as HCL (g) (g = gas phase), however, from 1250-1600 K a small amount of Cl (g) is also present (< 4%). From approximately 700 K to 300 K HCl decomposes gradually forming Cl₂ (g) instead. Sulphur is stable as SO₂ (g) and a minor amount of SO₃ (g) from 1600 to 1350 K. From 1350 K to 1250 K the stable phase changes to CaSO₄ (cr) (cr = solid phase) completely and this species remain stable until 300 K.

Arsenic. As is found stable as Ca₃(AsO₄)₂ (cr), when cooling the flue gas from 1300 K to approximately 300 K. From 1300 K to 1400 K the stable form of As gradually changes to

AsO (g). Above 1400 K, AsO (g) is the only stable phase of As. This means that As following the flue gas should condense and be captured corresponding to the efficiency of the ESP or fabric filter, provided sufficient residence time and specific surface area. Rigo and Chandler [14] observed this behaviour for As, where the major volatile fraction of As was captured in the fabric filter residue in the combustion plant, and less than 1 wt% escapes through the stack.

Cadmium. CdCl₂ (cr,l) is the stable phase in the lower temperature range from 300 to 600 K. From 600 K the stable phase changes sharply to CdCl₂ (g), which is stable until 1200 K. From 1200 K, the stable phase gradually changes to Cd (g) and a minor amount of CdO (g) (< 3% (mol/mol) from 1300 K) up to 1600 K. Similar to As, the volatile fraction of Cd should be captured in the ESP or fabric filter corresponding to the efficiency, assuming a temperature of 500 K, when entering the flue gas cleaning system (FGCS). However, 500 K is close to where Cd starts to condense and a slightly higher temperature might cause parts of Cd to pass through the FGCS and enter the stack. Cd may also condense on aerosols, which might not be captured by the filter system. Rigo and Chandler [14] found that 96 wt% of the volatile part of Cd is captured in the fabric filter, while Sørnum et. al. [12] found that 25 wt% of the volatile Cd escapes through the stack. The reason for this difference may be found in the fact that in the study of Rigo and Chandler, 96 wt% of Cd is volatile, while the corresponding value in the study of Sørnum et. al. is 41 wt%. In addition the concentration of Cd in the MSW is a factor of 2.4 higher in the study of Rigo and Chandler compared to the study of Sørnum et. al.. Given similar operational conditions and efficiencies of FGCS, this means that the concentration of Cd in the flue gas would be ~ 6 times higher. However, Hasselriis and Licata [15] stated that even a substantial spiking of Cd in the feed resulted in only marginal changes in stack emission. Given a constant stack

emission of Cd, means that a lower concentration of Cd in the flue gas will increase the fraction of Cd escaping through the stack. The relatively low temperature of condensation for Cd increases the possibility for condensation on aerosols, since aerosols are formed at low temperatures in the boiler.

Chromium. Cr is only significantly volatile at high temperatures, i.e. above 1500 K, where the amounts of gaseous oxides start to increase. $\text{CaO}\cdot\text{Cr}_2\text{O}_3$ (cr) is the dominant species from 300 to 1500 K. At 1600 K, ~ 40% (mol/mol) of the chromium is volatilised. In the study of Sørum et. al. [12], 99.6 wt% of Cr remained in the bottom ash. All significant amount of volatile chromium (0.4 wt%) of Cr was captured in the ESP. Rigo and Chandler [14] experienced the same behaviour with all significant volatile amount of Cr being captured in the FGCS and boiler hoppers. In other words, at 500 K, Cr is present in solid phase, as also the equilibrium calculations have shown.

Copper. There are three dominant stable phases for Cu. CuO (cr) is stable from 300 to 700 K, from where the amount of $(\text{CuCl})_3$ (g) gradually increases. $(\text{CuCl})_3$ (g) is the dominant species from 900 to 1200 K. From 900 K, the amount of CuCl (g) gradually increases and becomes the dominant species from 1200 to 1600 K. Minor amounts of CuO (g) and Cu (g) can be observed at high temperatures. Rigo and Chandler [14] showed that the major amount of the volatile fraction of Cu was captured on fly ash particles in the boiler hoppers (1/3) and in the fabric filter (2/3). At 500 K, the equilibrium calculations showed that Cu was present in solid phase as CuO (cr).

Mercury. Hg is stable in gas phase for the entire temperature range with two dominant stable phases. HgCl_2 (g) is the stable phase from 300 to 800 K, from where it gradually

shifts to Hg (g) and a small amount of HgO (g) (<1.8% (mol/mol)). Mercury is the most volatile of the metals in this study. Equilibrium calculations and experimental investigations confirm this. In the studies of Rigo and Chandler [14] and Sørum et. al. [12], almost all Hg was volatilised. In the study of Rigo and Chandler, a dry scrubbing system (lime injection) was used, capturing ~ 40 wt% of the volatile Hg. In the study of Sørum et. al. a wet scrubbing system was used and the corresponding capture of Hg was ~ 90 wt%. Although neither of the systems used in the two studies are specifically intended to remove mercury they have a removal effect. This indicates that the capture efficiency of Hg is closely related to the type of FGCS.

Nickel. Ni is present as the thermodynamically stable, condensed NiCl₂ (cr,l) in the temperature range 300-500 K. From 500 to 900 K, 2NiO.SiO₂ (cr) is the stable phase, which gradually decreases to zero from 900 to 1520 K, while the amount of NiCl₂ (g) increases, being the dominant species at higher temperatures. Minor amounts of NiCl (g) and Ni (g) (< 5% (mol/mol)) is observed above 1400 K. Of the 2 wt% of Ni in the study of Rigo and Chandler [14] not found in the bottom ash, approximately 60 wt% was captured on fly ash particles in the boiler hoppers while the remaining 40 wt% was captured in the fabric filter. The volatile fraction of Ni may be volatilised on the grate and consequently condensed and/or it might follow the fly ash. This confirms the non-volatile behaviour of Ni as shown from the equilibrium calculations.

Lead. The highly corrosive species PbCl₂ (cr,l) is the stable phase from 300 to 550 K, from 550 to 650 K the stable phase shifts to PbCl₂ (g). In the higher temperature range from 1100 to 1600 K, PbCl₂ (g) gradually decomposes, while the amount of PbO (g) increases and dominates above 1400 K. Minor amounts of PbCl (g) and Pb (g) (< 15% (mol/mol)) are

also observed in the higher temperature range. A calculation including PbCl_4 (g) showed that this species had a large influence on the equilibrium distribution. PbCl_4 (g) was the single significant stable species from 300 to 1200 K and the dominating species up to 1300 K. This volatile behaviour at low temperatures is not experienced in real combustion plants where most of the volatile Pb is captured on fly ash particles. Hence, PbCl_4 (g) was left out of the calculations. In the studies of Rigo and Chandler [14] and Sørum et. al. [12] almost all of the volatile Pb is captured on fly ash particles in the filter systems.

Zinc. Zn has a fairly complex equilibrium distribution. Starting with ZnCl_2 (cr,l) as the stable phase from 300 to 440 K, from where the stable phases is divided between ZnCl_2 (cr,l) and the silicate $2\text{ZnO}.\text{SiO}_2$ (cr) in a approximately 30/70 ratio up to 550 K. The amount of $2\text{ZnO}.\text{SiO}_2$ (cr) keeps stable at ~ 70% (mol/mol) up to 1570 K from where it gradually decreases to 55% (mol/mol) at 1600 K. From 550 to 980 K the remaining 30% (mol/mol) of Zn gradually shifts from the solid phase ZnO (cr) to the gaseous chloride ZnCl_2 (g) as the stable phase. The amount of ZnCl_2 (g) gradually decreases as the amount of Zn (g) increases from 1400 K. the studies of Rigo and Chandler [14] and Sørum et. al. [12] showed that the volatile fraction of Zn is condensed on fly ash particles and captured in the filter systems.

3.1 Influence of sulphur content

No significant change in equilibrium distribution or volatile behaviour is observed at S/S_{BC} ratios lower than 1.0. For calculations at a S/S_{BC} ratio of 1.5 and higher, the equilibrium distribution for all metals with the exception of Hg changes. Figure 2 shows how the distribution of As, Cd, Cr, Cu, Ni, Pb and Zn have changed at a S/S_{BC} ratio of 2.0. The stable phase is no longer $\text{Ca}_3(\text{AsO}_4)_2$ (cr) , but As_2O_5 (cr). As_2O_5 (cr) is more volatile than $\text{Ca}_3(\text{AsO}_4)_2$ (cr) making As fully volatilised at 860 K, instead of 1430 K for $\text{Ca}_3(\text{AsO}_4)_2$ (cr)

at base case conditions. As_4O_6 (g) is observed as an intermediate species between 810-960 K, before AsO (g) becomes the only stable phase. The explanation of the shift from $\text{Ca}_3(\text{AsO}_4)_2$ (cr) to As_2O_5 (cr) when increasing the S/S_{BC} ratio is found in the fact that at a S/S_{BC} ratio of 2.0 there is enough S to bind Ca as CaSO_4 (cr) completely, while at a S/S_{BC} ratio of 1.0 Ca is only partly bound as CaSO_4 (cr) and partly CaO (cr,l). As opposed to when Ca is bound only as CaSO_4 (cr), parts of Ca will bind as $\text{Ca}_3(\text{AsO}_4)_2$ (cr) in competition with CaO (cr,l).

Cd becomes less volatile when increasing the S/S_{BC} ratio from 1.0 to 1.5 due to the shift to the thermally more stable cadmium sulphate (CdSO_4 (cr)) from the less stable cadmium chloride (CdCl_2 (cr,l)) as the stable phase at lower temperatures. At base case conditions CdCl_2 (cr,l) is fully volatilised at 650 K, however at a S/S_{BC} ratio of 2.0, where CdSO_4 (cr) is the stable phase, Cd is fully volatilised at 870 K. The equilibrium distribution above 900 K is the same for both S/S_{BC} ratios. Cd gets slightly less volatile when increasing the S/S_{BC} ratio from 1.5 to 10 as CdSO_4 (cr) decomposes at higher temperatures.

The equilibrium distribution of Cr is strongly altered when increasing the S/S_{BC} ratio from 1 to 2, as can be observed in Figure 2. Instead of $\text{CaO}\cdot\text{Cr}_2\text{O}_3$ (cr) being the dominant stable phase with an increasing amount of chromium oxides at higher temperatures at base case conditions, a major change in the equilibrium distribution is observed. At lower temperatures chromium forms two hydrated sulphate compounds: $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3\cdot 2\text{H}_2\text{O}$ (cr) (below 350 K) and $[\text{Cr}_2(\text{H}_2\text{O})_6(\text{SO}_4)_3]\cdot 2\text{H}_2\text{O}$ (cr) (between 350 and 430 K). At 450 K, the solid non-hydrated sulphate, $\text{Cr}_2(\text{SO}_4)_3$ (cr), is formed and remains stable up to 770 K, from where Cr_2O_3 (cr) becomes the dominating stable phase. This distribution at lower temperatures is similar to the one Frandsen et. al. [8] reported for combustion of coal. At higher temperatures, however, the equilibrium distribution is different, one of the reasons being that $\text{CaO}\cdot\text{Cr}_2\text{O}_3$ (cr) was not included in the study of

Frandsen et. al. Starting from 770 K, Cr_2O_3 (cr) gradually decomposes, forming $\text{CrO}_2(\text{OH})_2$ (g). At 1240 K, however, a radical shift in equilibrium distribution occurs. The solid phase changes from Cr_2O_3 (cr) to $\text{CaO} \cdot \text{Cr}_2\text{O}_3$ (cr) and the amount of this species increases at the expense of $\text{CrO}_2(\text{OH})_2$ (g), up to 1430 K, from where it gradually decomposes into several gaseous chromium oxide species. The sudden shift of solid phase at 1240 K is connected to the decomposition of CaSO_4 (cr) into CaCl_2 (g). The decomposition of $\text{CaO} \cdot \text{Cr}_2\text{O}_3$ (cr) above 1430 K may be connected to the partial shift of the solid phase of Ca to CaO (cr,l).

The volatile behaviour of Cu is not significantly altered when increasing the S/S_{BC} ratio from 1.0 to 10. At low temperatures, CuSO_4 (cr) is the stable phase at a S/S_{BC} ratio from 1.5 and higher, with a narrow temperature area of CuO (cr) after CuSO_4 (cr) has decomposed fully (CuSO_4 (cr) \rightarrow CuO (cr) + SO_2 + $\frac{1}{2}$ O_2). Increasing the S/S_{BC} ratio from 1.5 to 10, CuSO_4 (cr) goes from being fully volatilised at 830 to 920 K. CuO (cr) is fully volatilised at 970 K at all S/S_{BC} ratios, but the temperature range where it is stable becomes narrower with higher S/S_{BC} ratio. Above temperatures of 970 K, the equilibrium distribution is not altered when varying the S/S_{BC} ratio.

Ni shows the same behaviour as was observed for Cu. The volatile behaviour is not altered when varying the S/S_{BC} ratio, but at lower temperatures (below 900-950 K), Ni is now stable as the solid sulphate, NiSO_4 (cr).

Pb, however, becomes less volatile with increasing S/S_{BC} ratio. The shift from PbCl_2 (cr,l) to PbSO_4 (cr,l) (observed at S/S_{BC} ratio from 1.5) as the stable solid phase increases the temperature where Pb is fully volatilised from 660 to \sim 900 K, as the sulphate is stable at higher temperatures than the chloride. A further increase in S/S_{BC} ratio from 1.5 to 10 increases the temperature where Pb is fully volatilised with 80 K.

Even though increasing the S/S_{BC} ratio from 1.0 to 1.5 shifts the stable phase of Zn at lower temperatures from chlorides and silicates to sulphates, the volatility is not largely

altered. However, at a S/S_{BC} ratio of 1.0 and lower, $ZnCl_2$ (g) is gradually increasing from 0 to 31% (mol/mol) from 510 to 980 K, while at S/S_{BC} ratio of 1.5 $ZnCl_2$ (g) is increasing from 0 to 31% (mol/mol) from 820 to 1020 K. Increasing the S/S_{BC} ratio further from 1.5 to 10 increases the temperature where the sulphate $ZnO \cdot 2ZnSO_4$ (cr) is fully decomposed from 1020 to 1110 K. Above 1100 K there is no significant difference in equilibrium distribution for Zn when varying the S/S_{BC} ratio. Especially for Pb and Zn the shift from condensed chlorides to sulphates at S/S_{BC} ratios equal or higher than 1.5 is important information since this may decrease deposit corrosion in the boiler [2].

3.2 Influence of chlorine content

As and Cr show no effect of a varying Cl/Cl_{BC} ratio. All other metals have to a varying degree effect of changing the Cl/Cl_{BC} ratio. Although the gaseous chlorides decompose at higher temperatures when increasing the Cl/Cl_{BC} ratio for Cd, Hg and Pb, there is no effect on the volatile behaviour. Cu, Ni and Zn become more volatile with increasing Cl/Cl_{BC} ratio. Increasing the Cl/Cl_{BC} ratio from 1.0 to 10 lower the temperature where Cu, Ni and Zn are fully volatilised from 970, 1520 and 1670 K to 670, 1000 and 780 K, respectively. A lower temperature of condensation will increase the possibility of heavy metal species condensing on very small particles or aerosols, which might escape the filter system and consequently be emitted through the stack.

3.3 Influence of fly ash content

Increasing the ash/ash_{BC} ratio from 1.0 to 2.0 does only have effect on the equilibrium distribution for Zn. $2ZnO \cdot SiO_2$ (cr) becomes more dominant on the expense of $ZnCl_2$ (cr,l), CuO (cr) and $ZnCl_2$ (g), below 1500 K. Decreasing the ash/ash_{BC} ratio, however, give significant changes in the equilibrium distribution for all metals with the only exception of Hg. The changes are similar to those described when increasing the S/S_{BC} ratio to 1.5 or

higher, were a shift from heavy metal chlorides to sulphates was observed at lower temperatures. Hence reducing the flyash content may reduce corrosion in deposits due to the shift from Pb and Zn chlorides to sulphates.

3.4 Influence of air/fuel ratio (λ)

The only significant effect of changing λ from 1.1 to 1.9, is that Cu becomes slightly less volatile (temperature where CuO (cr) is fully volatilised increases from 870 to 970 K) and that Cr becomes slightly more volatile. Cr becomes more volatile because increasing the excess air number will force $\text{CaO} \cdot \text{Cr}_2\text{O}_3$ (cr) to decompose into gaseous chromium oxides in order to maintain equilibrium.

4. CONCLUSIONS

As for the first part of this study, the lack of knowledge on the fate of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn at typical conditions for MSW combustion has motivated this work. The first part of this, which focused on the devolatilisation on the grate, and this part, which focuses on the condensation during cooling in the boiler, is closely related. The overall picture will give more information on the overall fate of heavy metals in MSW combustion. The fate of these metals as they go from the furnace to the filter has been studied using equilibrium calculations. The heavy metals behaved differently with respect to condensation at combustion conditions in a MSW grate furnace. The heavy metals also responded differently to changes in MSW composition and operational parameters. Thus, no overall conclusion applicable to all heavy metals is provided.

Investigation of the condensing behaviour of the heavy metals as they pass through the boiler and enter the flue gas cleaning system on their way to the stack (500–300 K), revealed that only Hg was present in gas phase.

Increasing the Cl/C_{BC} ratio from 1.0 to 10 lower the temperature where Cu, Ni and Zn are fully volatilised from 970, 1520 and 1670 K to 670, 1000 and 780 K, respectively. A lower temperature of condensation will increase the possibility of heavy metal species condensing on very small particles or aerosols, which might escape the filter system and consequently be emitted through the stack.

Solid phase interaction between As and Cr with Ca and silicates of Ni and Zn were identified. In the case of As at oxidising conditions, the formation of Ca₃(AsO₄)₂ (cr) was dependent on the S/Ca ratio. A high S/Ca ratio, which is obtained by a high sulphur content or low concentration of fly ash in the flue gas, will favour the formation of As₂O₅ (cr) rather than the less volatile Ca₃(AsO₄)₂ (cr). A low S/Ca ratio will on the other hand favour the formation of Ca₃(AsO₄)₂ (cr).

Another important consequence of increasing the sulphur/chlorine ratio in the flue gas (S/S_{BC} ratios equal or higher than 1.5), is the shift from solid phase metal chlorides to sulphates for Cd, Cr, Cu, Ni, Pb and Zn at lower temperatures. In the case of Pb and Zn, a shift from the highly corrosive species PbCl₂ (cr,l) and ZnCl₂ (cr,l) to PbSO₄ (cr) and ZnSO₄ (cr) may reduce corrosion in the boiler sections significantly in a combustion plant for MSW. Increasing the sulphur/chlorine ratio in the flue gas may be obtained by removing waste with high chlorine content such as PVC, or reducing the fly ash content. At high fly ash content the sulphur is bound to the ash as CaSO₄ (cr) up to 1300 K. Reducing the fly ash content will increase the amount of available sulphur to form heavy metal sulphates.

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Table 1. Elemental composition of fuel and oxidiser for “ base case” calculations and waste composition.

Input parameters	Flue Gas (Oxidising conditions)	Waste composition
C	32.7 mole	25.29 wt%
H	80.2 mole	3.39 wt%
O	172.3 mole	18.06 wt%
N	530.8 mole	0.48 wt%
S	0.08 mole	0.17 wt%
Cl	0.25 mole	0.56 wt%
l	1.9	
Ash	0.8 wt%	27.24 wt%
Temperature	300-1600 K	
Moisture		24.82 wt%
Al	0.007 mole	
Ca	0.103 mole	
Fe	0.065 mole	
Si	0.009 mole	
As	$2.430 \cdot 10^{-4}$ mole	18.2 ppmw
Cd	$3.637 \cdot 10^{-4}$ mole	40.9 ppmw
Cr	$1.072 \cdot 10^{-3}$ mole	55.7 ppmw
Cu	$7.290 \cdot 10^{-3}$ mole	462.9 ppmw
Hg	$5.615 \cdot 10^{-6}$ mole	1.1 ppmw
Ni	$4.843 \cdot 10^{-4}$ mole	28.4 ppmw
Pb	$6.565 \cdot 10^{-4}$ mole	136.0 ppmw
Zn	$2.620 \cdot 10^{-2}$ mole	1713.7 ppmw

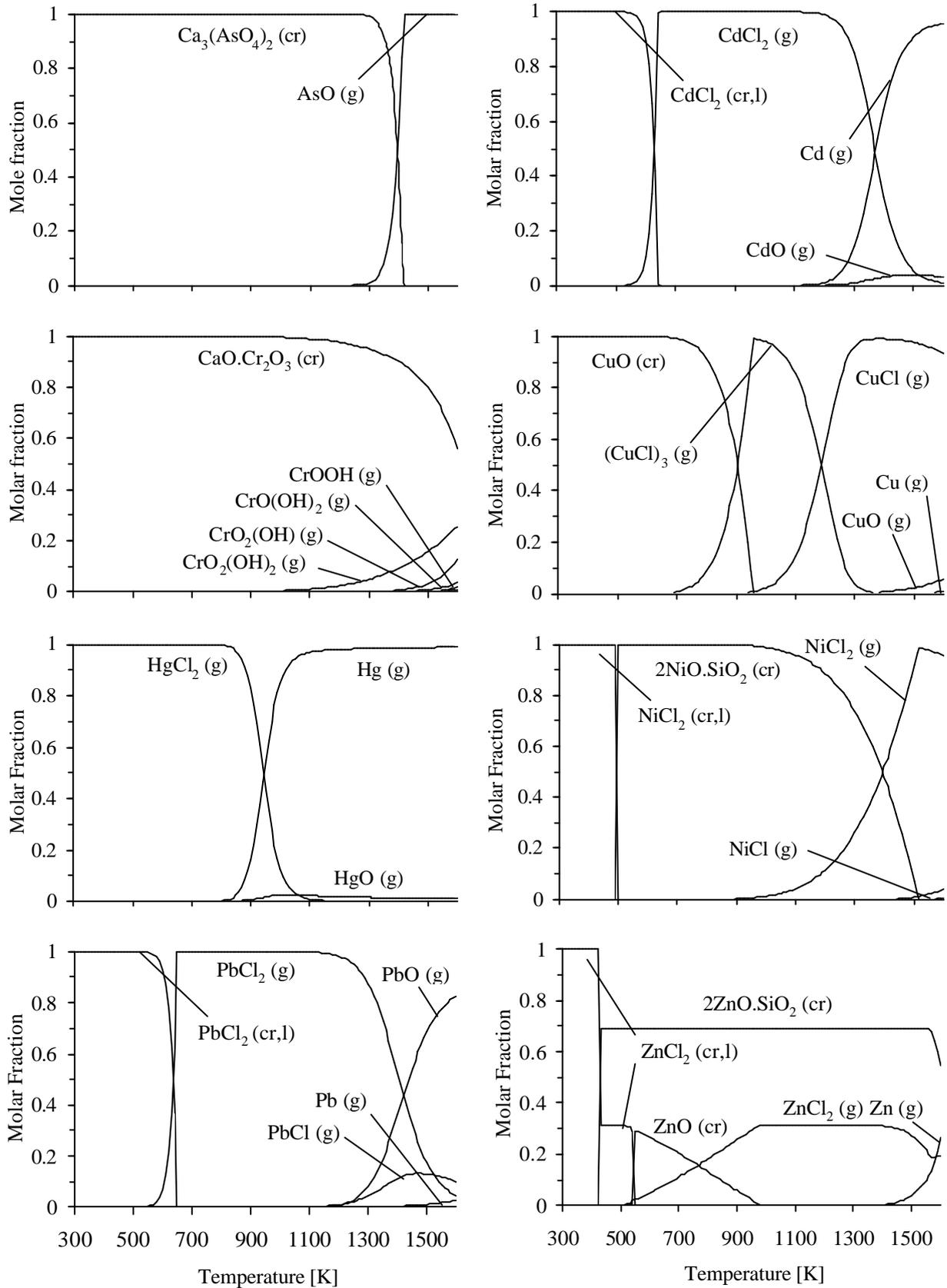


Figure 1. Equilibrium distribution of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn at oxidising conditions in the flue gas. $\lambda = 1.9$.

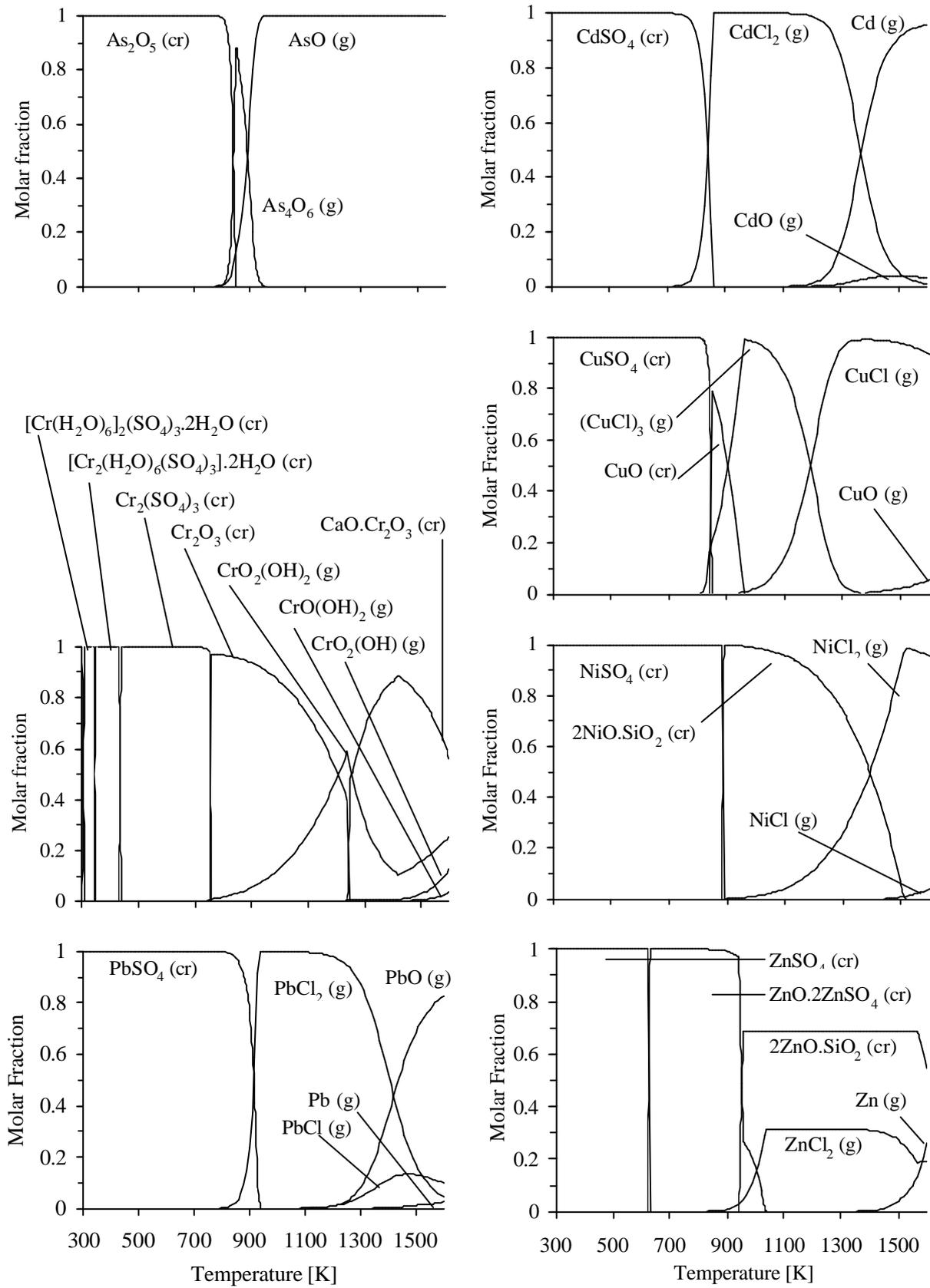


Figure 2. Equilibrium distribution of As, Cd, Cu, Cr, Ni, Pb and Zn at a S/S_{BC} ratio of 2.0.

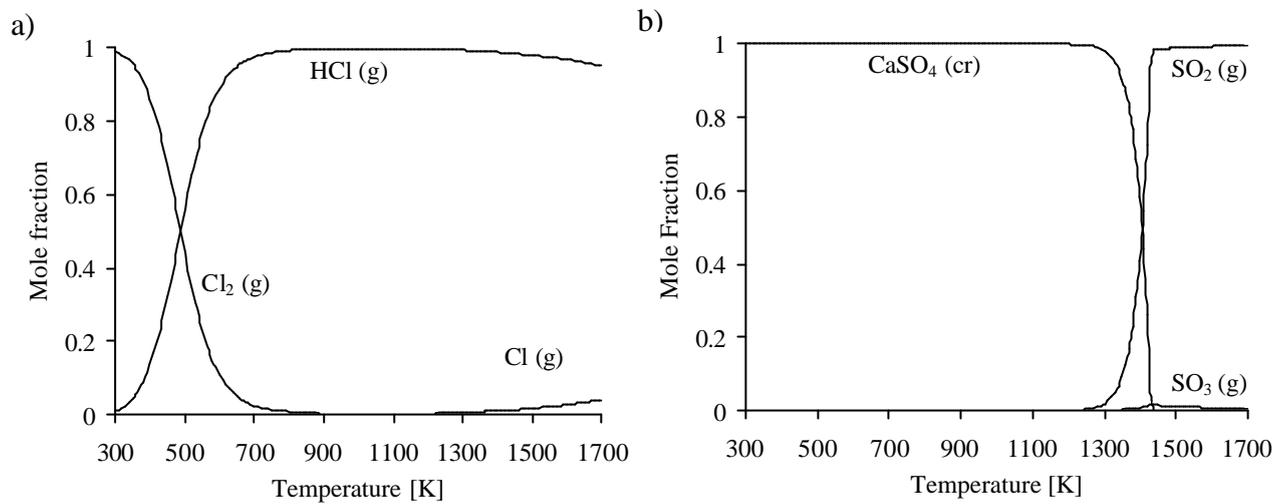


Figure 3. Chlorine and sulphur balance for at base case conditions. a) Chlorine and b) Sulphur.