

# **On the Fate of Heavy Metals in Municipal Solid Waste Combustion Part I: Devolatilisation of Heavy Metals on the Grate**

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## **ABSTRACT**

The aim of this study has been to investigate the chemistry and volatility of the heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn on the grate of a MSW fired furnace, using equilibrium calculations. Focus has been on the influence of varying MSW composition and operational parameters such as air/fuel ratio and temperature. Equilibrium distributions at 950-1600 K, under reducing and oxidising conditions on the grate, showed that Cd, Hg and Pb are fully volatilised. However, Cr is found to be stable in solid phase, in the entire temperature range. The volatile behaviour of Cd, Cr, Hg and Pb show no significant influence, while As, Cu, Ni and Zn are strongly influenced by one or more of the parameters; temperature, fuel/air and chlorine/metal ratios.

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

## 1. INTRODUCTION

The large amounts and inhomogeneous nature of municipal solid waste (MSW) combined with the awareness of environmental consequences connected to waste disposal have led to development of complex waste management systems. Material reuse and recycling, anaerobic digestion, composting and combustion with energy recovery are some of the methods that are used in addition to landfills. Paper, plastics, wet organic waste (wood, grass, food wastes, etc.) are the major components of the combustible fraction of MSW. However, the composition of the waste subject to energy recovery can vary largely between countries and within each country depending on factors such as standard of living and waste management policy. This variation in composition of the fuel may influence the operational parameters of combustion plants and alter the formation and emission of pollutant species.

One of the challenges and concern in MSW combustion is the emission of heavy metals [1]. Heavy metals may be harmful to the environment and humans when exposed to concentrations above what can be found in the natural environment. The heavy metal concentration in MSW compared to other solid fuels such as biomass and coal is relatively high [2-4] and in addition to that, variations in heavy metal concentrations in MSW are large, also within each fraction of MSW [5-7]. Heavy metals in MSW combustion may evaporate, react or show no response [8]. In order to decrease emissions of heavy metal species to the environment from any of the mass flows coming from a combustion plant for MSW (i.e. flue gas, fly ash, bottom ash, etc.), knowledge is needed on the behaviour of heavy metals in the combustion zone on the grate and in the flue gas from the furnace to filter. 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 land filling. 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. The first part of this study is concerned with the devolatilisation and chemistry of heavy metals on the grate.

Several studies using equilibrium calculations to investigate the behaviour of heavy metals in combustion systems have been performed. Equilibrium analysis has been used for studying trace elements in methane combustion [9], waste combustion [10, 11], coal gasification and combustion [12,13]. Common for all the above-mentioned work on equilibrium distribution of heavy metals in thermal fuel conversion systems is that no ash species are included. Ash species 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. In addition, more knowledge and understanding of the distribution and chemical composition of heavy metals under the conditions of MSW combustion is needed. The objective of this study is therefore to investigate the influence of varying operational parameters and MSW compositions on the devolatilisation and chemical composition of various heavy metals at typical combustion conditions in a grate furnace. Ash species are included to investigate possible interactions between heavy metals and ash species. Focus is on the influence of temperature, Cl/metal, S/metal and air/fuel ratios.

## 2. CALCULATION METHOD

The program MINGTSYS [12] was used for the global chemical equilibrium analyses. The program minimises the total Gibbs energy ( $G(T)$ ) for a given system of selected species. Thermodynamic data were taken from the GFE-DBASE version 2.0. The Gibbs free energy function is defined as:

$$GFE_i(T) = - \left( \frac{G_i^0(T) - H_{298,i}^0}{T} \right) \quad (1)$$

In Eq. 1,  $G_i^0$  is the standard Gibbs free energy for component  $i$ ,  $H_{298,i}^0$  is the enthalpy at 298 K for component  $i$  and  $T$  is the temperature. GFE functional expressions (eq. (1)) are used to calculate  $G(T)$ . Further documentation on the GFE-DBASE is described by Frandsen et al. [14]. Global equilibrium analysis (GEA) has several limitations when used on a combustion system. The residence time need to be long enough, or the temperature must be high enough, to ensure that all reactions reach equilibrium. A turbulent flame may introduce local conditions e.g. temperature and/or composition gradients which are not taken into account in a GEA. Physical adsorption, chemisorption and capillary condensation phenomena are not taken into account. No mixing models, in order to describe non-ideal behaviour between heavy metals and ash species, have been used in this study. The reason for not using an overall applicable mixing model that will give a description of how heavy metals and heavy metals and ash species mix is that at present no such model exists. The mode of occurrence of the heavy metal in the fuel also influence the volatility [3]. A volatile heavy metal, which normally should be released from the fuel and found in the flue gas, could stay in the bottom ash if the metal is bound in a silicate rather than organically. In spite of the above-mentioned limitations, the method of determining stable phases, assuming global equilibrium, is at present the only computational possibility for generating knowledge about the chemistry of heavy metals in combustion systems. Another reason for using GEA on thermal conversion systems is the lack of kinetic data for heavy metal reactions. Few thermodynamic data are available for species containing more than one heavy metal. Verhulst [10] and Ljung and Nordin [15] showed that there were no interaction between arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). These are the same heavy metals as considered in this study, therefore, each heavy metal has been considered separately. Including all relevant species involved in the combustion process and using the best available

thermodynamic data is important, otherwise the results may be misleading [3]. Frandsen et. al. [16] compared four different thermodynamic packages for calculation of equilibrium distribution for the oxidative thermal conversion of coal. The major differences between the four thermodynamic packages were caused by differences in the list of species included and in the thermodynamic data.

A comparison of *trends* observed from experimental investigations in literature with GEA on the volatile behaviour on the grate by performing a comprehensive parametric study will be performed. In addition, generating additional knowledge on heavy metal chemistry in MSW combustion is another important aspect of this work.

A comprehensive list of ash and heavy metal species and possible interactions between ash components and heavy metals are included in these investigations. Included are the heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, Zn and the ash species Aluminium (Al), Calcium (Ca), Iron (Fe) and Silicone (Si). Ash species have only been included to make interactions between ash species and heavy metals possible. Other ash species such as Potassium (K), Natrium (Na) and Phosphorous (P) could have been included as they might compete with the heavy metals on the access to sulphur (S) and chlorine (Cl). However, the access to S and Cl for the heavy metals is investigated by performing a parametric study varying the content of S and Cl. The distribution of ash species is not subject to any discussion in this work unless there is an interaction with any of the heavy metals.

In order to come up with two systems for equilibrium calculations, one for *reducing* conditions and one for *oxidising* conditions, a comprehensive set of species were included in the initial calculations using a typical ultimate composition for MSW. After a reduction of the original set of species to include only the species that were actually involved in the equilibrium chemistry (even at very small concentrations), two sets of species were

established, one for reducing conditions and one for oxidising conditions. The combustion products, ash and heavy metal species are listed in the Appendix in Tables 1-3.

### **3. INPUT PARAMETERS AND PARAMETRIC STUDY**

A “typical” composition for European/US MSW has been used to calculate the elemental and heavy metal concentrations. The composition being 33.1 wt% of paper and cardboard, 6.5% plastics, 24.4% wet organic waste, 6.4% glass, 3.7% metals, 12.6% of other combustibles (wood, rubber, leather, textiles) and a rest fraction of 13.3% (ash, sand, stones, fines, etc). Table 4 shows the ultimate analysis and heavy metal concentrations for the chosen composition of MSW based on literature values [6,7,17]. The conditions investigated in this study reflect those of a commercial grate furnace. Details of typical grate furnaces and flue gas cleaning systems (FGCS) are provided by Sørum et. al. [18] and Rigo and Chandler [7]. Table 5 shows the elemental composition of fuel and oxidiser for base case (BC) calculations. The only difference between the reducing and oxidising conditions on the grate is the air/fuel ratio.

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. No significant influence on the equilibrium distribution was found when performing calculations with MSW versus RDF on the grate. 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  $Cl/C_{BC}$  and  $S/S_{BC}$  ratios denote the actual number of moles of Cl or S 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% and 0.02 and 1.7 wt%, respectively (i.e.  $Cl/C_{BC}$  and  $S/S_{BC}$  ratios between 0.1 to 10) for both reducing and oxidising conditions. The air/fuel ratio ( $\lambda$ ) was varied between 0 and 0.9 for reducing conditions and 1.2 and 1.9 for oxidising conditions.

#### **4. RESULTS AND DISCUSSION**

Previous experimental studies have shown large variations in partitioning in similar incinerators for MSW for the eight heavy metals focused upon in this study. These large variations in volatile behaviour may be explained by several factors such as variations in MSW composition, operational conditions and measurement techniques and methods. The work presented here will focus on the volatile behaviour and chemical composition of metals on the grate at temperatures between 950 and 1600 K. An adiabatic flame temperature of ~ 1500 K was calculated using the base case fuel composition and  $\lambda = 1.9$ . In addition, Gort [19] 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. The lower temperature (950 K) on the grate reflects the point where all components of MSW are volatilised and only fixed carbon is left.

Calculations simulating conditions on the grate using both a reducing and an oxidising system have been performed at base case conditions. The results from these base case calculations are shown in Figure 1 for reducing conditions and in Figure 2 for oxidising conditions. 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 distribution for base case calculations for reducing and oxidising conditions on the grate and oxidising conditions in the flue gas are shown in



Figure 4 in the Appendix. At base case reducing conditions, chlorine is present as  $\text{CaCl}_2$  (cr) (cr = solid phase) and gaseous  $\text{HCl}$  (g) (g = gas phase) up to 1050 K. From 1050 K,  $\text{HCl}$  (g) is the dominating species, whereas for oxidising conditions,  $\text{HCl}$  (g) is the dominating species with minor amounts of  $\text{Cl}$  (g) (< 1.5% (mol/mol)) at higher temperatures. The sulphur distribution for reducing conditions is dominated by  $\text{CaS}$  (cr) and  $\text{H}_2\text{S}$  (g) up to 1270 K, from where  $\text{H}_2\text{S}$  (g) is the dominating species. Minor amounts of  $\text{COS}$  (g),  $\text{SO}_2$  (g) and  $\text{HS}$  (g) (< 3.5% (mol/mol)) are also observed. The sulphur distribution for oxidising conditions is completely different.  $\text{CaSO}_4$  (cr) is the stable phase below 1250 K, from where it gradually changes to  $\text{SO}_2$  (g), which is the dominating S-containing species above 1400 K.

**Arsenic.** Under reducing conditions, As is present as  $\text{AsO}$  (g) with only a small amount of  $\text{As}_2$  (g) (< 3.5% (mol/mol)) below 1050 K. Under oxidising conditions, however, As is stable as  $\text{Ca}_3(\text{AsO}_4)_2$  (cr) up to approximately 1300 K. From 1300 K to 1400 K the stable form of As gradually changes to  $\text{AsO}$  (g). The difference may be explained by the equilibrium distribution of Ca. Under reducing conditions the dominant Ca species is  $\text{CaO}$  (cr), whereas under oxidising conditions the dominant species is  $\text{CaO}$  (cr,l) (cr,l = condensed liquid phase). In order to test the hypothesis that the Ca distribution determines the interaction between As and Ca,  $\text{CaO}$  (cr), was removed from the calculations for reducing condition. After the removal of  $\text{CaO}$  (cr), Ca was bound as  $\text{CaO}$  (l) and minor amounts of  $\text{CaCl}_2$  (cr) and  $\text{CaS}$  (cr). In this latter case  $\text{Ca}_3(\text{AsO}_4)_2$  (cr) was present at lower temperatures (below 1000 K) together with  $\text{AsO}$  (g). Removing  $\text{CaO}$  (l) in addition to  $\text{CaO}$  (cr) resulted in a similar equilibrium distribution as observed for oxidising conditions. Verhulst et. al. [10] found that  $\text{As}_2\text{O}_5$  (cr), was the stable phase up to about 800 K, from where it volatilises between 800 and 1300 K to  $\text{As}_4\text{O}_6$  (g). Above 1300 K  $\text{AsO}$  (g) was the

dominant species. Frandsen et. al. [12] found similar results as Verhulst under the conditions of coal combustion, however  $\text{As}_4\text{O}_6$  (g) was only present between 750 to 900 K, from where  $\text{AsO}$  (g) becomes the stable species. Wu and Biswas [9] found that the equilibrium distribution for As in an oxidising system was  $\text{As}_2\text{O}_5$  (cr) at lower temperatures and  $\text{AsCl}_3$  (g) at higher temperatures. However, Verhulst, Frandsen and Wu did not include  $\text{Ca}_3(\text{AsO}_4)_2$  (cr) in their studies. In addition, Wu did not include  $\text{As}_4\text{O}_6$  (g) in his study. Rigo and Chandler [7] found that 50 wt% of As remained in the bottom ash during combustion of MSW in a grate combustion system. This indicates that the volatility of As is strongly dependent upon the MSW composition and operational parameters such as air/fuel ratio and temperature.

**Cadmium.**  $\text{Cd}$  (g) is the stable phase for Cd under reducing conditions at 950-1600 K. At oxidising conditions the stable phase is  $\text{CdCl}_2$  (g) up to approximately 1150 K, where it gradually changes to  $\text{Cd}$  (g) and a minor amount of  $\text{CdO}$  (g) (< 2 % (mol/mol)) up to 1600 K. These distributions are fairly “classical” and has been observed also for coal gasification and combustion as reported by Frandsen et. al. [12]. Ljung and Nordin [15] also reported similar equilibrium distribution behaviour during combustion of biomass. No significant interaction between ash species and Cd could be detected. The distribution of Cd among  $\text{Cd}$  (g),  $\text{CdO}$  (g) and  $\text{CdCl}_2$  (g) is governed by the reactions:  $\text{CdCl}_2$  (g) +  $\text{H}_2\text{O}$  (g)  $\rightleftharpoons$   $\text{CdO}$  (g) +  $2\text{HCl}$  (g) and  $\text{CdO}$  (g)  $\rightleftharpoons$   $\text{Cd}$  (g) +  $\frac{1}{2}\text{O}_2$  (g), where  $\text{CdO}$  (g) will dissociate into  $\text{Cd}$  (g) and  $\text{O}_2$  (g) at temperatures above 1000 K according to Frandsen et. al. [12].

The literature reports very varying degree of volatility of Cd in real grate combustion plants for MSW. Several studies on similar grate combustion plants for MSW, reports the extremes of Cd volatile fraction to be between 17 to 83 wt% [7,20]. This varying degree of

volatilisation is not observed in this work, as Cd is entirely volatilised in the investigated temperature range. Water-cooled grates [18] versus air-cooled grates [7], causing a lower temperature on the grate, may be one of the reasons for the large variations in the volatile behaviour of Cd.

**Chromium.** Cr does only to a very small degree volatilise under the given temperature range. This is also observed in practice in real combustion plants, where Rigo and Chandler [7] and Sørnum et. al. [18] states that ~ 95 wt% of Cr will remain in the bottom ash.  $\text{CaO}\cdot\text{Cr}_2\text{O}_3$  (cr) is the dominant species for both reducing and oxidising systems, with small amounts of oxides (< 10 % (mol/mol)) are formed starting at approximately 1250 K for the oxidising system. In the reducing system, the  $\text{CrOOH}$  (g) oxide is barely present above 1550 K. The equilibrium distribution for Cr is not significantly influenced changing from reducing to oxidising conditions.

**Copper.** The volatile behaviour for Cu is largely altered when changing from reducing to oxidising conditions. At reducing conditions, Cu is present as sulphides in solid phase as  $\text{CuS}\cdot\text{FeS}$  (cr) (up to 1200 K) and  $\text{Cu}_2\text{S}$  (cr,l) (from 1200 K). A gradual increase in the chloride  $\text{CuCl}$  (g) is observed from approximately 1200 K, up to approximately 50% (mol/mol). From 1350 K, the amounts of  $\text{Cu}$  (g) and  $\text{CuH}$  (g) increases up to a maximum of 45 and 15% (mol/mol) at 1600 K, respectively. At oxidising conditions Cu is only present in gas phase. First as  $(\text{CuCl})_3$  (g), which gradually decomposes to  $\text{CuCl}$  (g) from 950 K. Minor amounts of  $\text{CuO}$  (g) and  $\text{Cu}$  (g) (< 4% (mol/mol)) can be observed at higher temperatures (above 1450 K). The results found for oxidising conditions are similar to those found by Verhulst et. al. [10] at typical conditions for MSW combustion. Values found in the literature reports that 89–96 wt% of Cu remained in the bottom ash [7,21].

**Mercury.** Hg is present only in gas phase for both reducing and oxidising conditions. The distribution of species, however, is different. At reducing conditions, only Hg (g) is present, while at oxidising conditions up to 28% (mol/mol) of HgCl<sub>2</sub> (g) is observed in the lower temperature range (below 1100 K). However, Hg (g) is the dominant species at oxidising conditions as well. A small amount of HgO (g) (< 1% (mol/mol)) is also observed for the entire temperature range. The difference between the reducing and the oxidising system can be found by looking at the Cl distribution. Cl in the reducing system is partly bound as CaCl<sub>2</sub> (cr) up to 1050 K from where HCl is the only significant species. This means that in competition with HCl (g) for chlorine, mercury does not form chlorides. In competition with CaCl<sub>2</sub> (cr), however, mercury chloride is formed. The equilibrium distribution for oxidising conditions is “classical” and has been found by other researchers such as Frandsen et. al. [12] and Verhulst et. al. [10] for coal and waste combustion, respectively. Experimental studies on the volatile behaviour of Hg in grate combustion plant states that up to 19 wt% will remain in the bottom ash [7,20]. The relatively large amount of Hg remaining in the bottom ash in some studies may be found in unburned fractions of the fuel.

**Nickel.** The major part of Ni is present as the stable condensed elemental nickel Ni (cr,l), for the reducing system at 950-1600 K. Small amounts (< 10% (mol/mol)) of chlorides in gas phase and Ni (g) is observed above 1400 K. Under oxidising conditions the dominant species is 2NiO.SiO<sub>2</sub> (cr). However, increasing amounts of chlorides in gas phase, especially NiCl<sub>2</sub> (g), is observed already at 950 K, with a maximum of approximately 80% (mol/mol) at 1600 K. The availability of oxygen may explain the formation of 2NiO.SiO<sub>2</sub> (cr) in the oxidising system rather than Ni (cr,l) as observed in the reducing system, since Si

is bound as  $\text{SiO}_2$  (cr,l) for both systems. Rigo and Chandler [7] found that 98 wt% of Ni remained in the bottom ash.

**Lead.** The distribution of Pb under reducing and oxidising conditions is quite different. At lower temperatures ( $<1050$  K), at reducing conditions, Pb (g) and lead chlorides are dominating. Above 1050 K, the amount of Pb (g) gradually increases on the expense of lead chlorides. An increasing amount of PbS (g) is observed up to approximately 1270 K, from where it starts to gradually decrease with increasing temperature. The sharp edges observed in the  $\text{PbCl}_k$  (g) curves at 1050 K may be explained by looking at the chlorine availability for the system. At 1050 K the solid phase  $\text{CaCl}_2$  (cr) disappears and chlorine is present as HCl (g). As for Hg, the formation of chlorides of Pb in competition with HCl (g) as opposed to  $\text{CaCl}_2$  (cr) will decrease with increasing temperature.  $\text{PbCl}_4$  (g) was added in an additional calculation for the reducing system, but no influence was found. In the oxidising system  $\text{PbCl}_2$  (g) is the stable phase at temperatures below 1150 K. From approximately 1150 K an increasing amount of PbO (g) and PbCl (g) is observed. A minor amount of Pb (g) ( $< 5\%$  (mol/mol)) is observed from approximately 1400 K. In order to check the possible influence of  $\text{PbCl}_4$  (g) on the equilibrium distribution of Pb this species was added in an additional calculation. This calculation showed that  $\text{PbCl}_4$  (g) was the dominating species up to about 1300 K. However,  $\text{PbCl}_4$  (g) was also the only Pb species at room temperature (300 K) and was therefore excluded from these calculations. The literature shows a large variation in the volatility of Pb. Reported extreme values of the fraction of Pb remaining in the bottom ash, varied from 58-94 wt% [18,21,22]. Srinivasachar et. al [23] stated that the use of an additive (no description of the additive was given) gave very promising results for controlling lead aerosol emissions and minimising lead chloride deposition due to decreased volatility.

**Zinc.** At 950 K the silicate  $2\text{ZnO}\cdot\text{SiO}_2$  (cr) is the dominant species under reducing conditions. However, it gradually decreases with increasing temperature to zero at 1100 K, from where Zn (g) is the dominant stable phase. A minor amount of  $\text{ZnCl}_2$  (g) is observed from 950 to 1250 K. Under oxidising conditions,  $2\text{ZnO}\cdot\text{SiO}_2$  (cr) is the dominant species for the entire temperature range. However, Zn (g) is sharply increasing from 1450 K to 1600 K to a maximum of 26% (mol/mol). A minor amount of  $\text{ZnCl}_2$  (g) (< 10% (mol/mol)), linearly increasing from 950 to 1600 K is also observed. The difference between reducing and oxidising condition is related to the oxidation of Zn into  $2\text{ZnO}\cdot\text{SiO}_2$  (cr). Lowering the excess air will force  $2\text{ZnO}\cdot\text{SiO}_2$  (cr) to decompose into Zn (g) and  $\text{O}_2$  (g) in order to maintain the equilibrium. The experimental work of Rigo and Chandler [7] and Sørum et. al. [18] showed that 37-86 wt% of Zn remained in the bottom ash. Since chlorides of Zn in deposits are highly unwanted in the boiler, efforts should be made to decrease the volatility for Zn on the grate. The influence of different parameters such as temperature, availability of sulphur and chlorine and fuel/air ratio on the volatility is therefore of great importance for Zn.

#### **4.1 Influence of sulphur content**

The  $\text{S}/\text{S}_{\text{BC}}$  ratio was varied from 0.1 to 10 on a molar basis, keeping all other concentrations constant as given by base case composition. No changes in the distribution of heavy metal species were observed for the oxidising system when varying the  $\text{S}/\text{S}_{\text{BC}}$  ratio from 0.1 to 10. In the reducing system, only Cu, Ni and Pb experienced changes in equilibrium distribution.

As shown in Figure 3, a less volatile behaviour is observed for Cu with increasing  $\text{S}/\text{S}_{\text{BC}}$  ratio.  $\text{Cu}_2\text{S}$  (cr,l) becomes more and more dominant in the higher temperature range (1400

to 1600 K) on the expense of CuCl (g), Cu (g) and CuH (g). At a  $S/S_{BC}$  ratio of 0.1,  $Cu_2S$  (cr,l) is fully volatilised at 1480 K. At a  $S/S_{BC}$  ratio of 10, however, there is still 26% (mol/mol) left in the condensed phase at 1600 K. Only a minor increase is observed for CuS (g) in the temperature range 1500 to 1600 K at high  $S/S_{BC}$  ratios. At a  $S/S_{BC}$  ratio of 0.1,  $Cu_2S$  (cr,l) is also dominant in the lower temperature range, with a minor amount of CuS.FeS (cr) present.

The only significant effect on the equilibrium distribution of Ni, when varying the  $S/S_{BC}$  ratio is a shift from Ni (cr,l) to  $Ni_3S_2$  (cr,l) at approximately 1520 K for a  $S/S_{BC}$  ratio above 3. The volatile behaviour of  $Ni_3S_2$  (cr,l), however is similar to Ni (cr,l) at lower  $S/S_{BC}$  ratios.

For Pb the distribution of chlorides PbCl (g) and  $PbCl_2$  (g) stay constant when varying the  $S/S_{BC}$  ratio from 0.1 to 10. The amount of PbS (g) increases on the expense of Pb (g) as the  $S/S_{BC}$  ratio increases, however there is always more Pb (g) in the system than PbS (g).

## 4.2 Influence of chlorine content

The influence of the  $Cl/C_{BC}$  ratio gave different results for the reducing and oxidising systems and is therefore discussed separately.

### 4.2.1 Reducing system

The equilibrium distribution of As, Cd, Cr and Hg in the reducing system is not influenced by a changed content of Cl compared to base case.

Cu becomes more volatile when the  $Cl/C_{BC}$  ratio increases. At a 0.1  $Cl/C_{BC}$  ratio, 13% (mol/mol) of Cu is still in solid phase as  $Cu_2S$  (cr,l) at 1600 K, a significant amount of Cu (g) and minor amounts of CuCl (g), CuH (g) and CuS (g) are observed above 1500 K.

At a  $Cl/C_{BC}$  ratio of 10, however,  $Cu_2S$  (cr,l) is fully volatilised at 1420 K. At this ratio the chloride  $CuCl$  (g) is sharply increasing from 1200 K, and becomes the dominant species above 1400 K. Minor amounts of  $Cu$  (g) and  $CuH$  (g) is also observed in the higher temperature range from approximately 1400 K. It is interesting to observe that when increasing the  $Cl/C_{BC}$  ratio from 0.1 to 10, Cu becomes more volatile, which is the inverse effect on the volatile behaviour of Cu for a similar increase in the  $S/S_{BC}$  ratio. One should, however, be aware of the combined effect of  $S/Cl$  ratio. When the  $S/S_{BC}$  ratio is changed from 0.1 to 10 or the  $Cl/C_{BC}$  ratio is changed from 10 to 0.1, this corresponds to a change in the  $S/Cl$  ratio from 0.034 to 3.4. However, the investigation of the combined effect of  $S/Cl$  ratio is beyond the scope of this study.

Ni also becomes more volatile when increasing the  $Cl/C_{BC}$  ratio from 0.1 to 10. At a  $Cl/C_{BC}$  ratio of 0.1 and a temperature of 1600 K, 90% (mol/mol) of Ni is stable as Ni (cr,l), with minor amounts of Ni (g) and NiCl (g) (<10% (mol/mol)) present. Increasing the ratio to 10, causes Ni (cr,l) to be fully volatilised at 1450 K and chlorides to dominate the equilibrium distribution at temperatures above 1400 K.

Even though Pb is present in gas phase for all  $Cl/C_{BC}$  ratios, the equilibrium distribution changes. At  $Cl/C_{BC}$  ratios below 1.0, the distribution of Pb is dominated by Pb (g) and PbS (g), and below 1250 K also PbCl (g). Increasing the  $Cl/C_{BC}$  ratio above 1.0 leads to an increase in the amount of the lead chlorides PbCl (g) and PbCl<sub>2</sub> (g). However, Pb (g) is still the dominating species above 1450 K.

The volatile behaviour of Zn is not significantly altered even when changing the  $Cl/C_{BC}$  ratio from 0.1 to 10. However, the amount of ZnCl<sub>2</sub> (g) increases with increasing  $Cl/C_{BC}$  ratio on the expense of Zn (g), especially below 1400 K. Zn (g) is the dominating species at all  $Cl/C_{BC}$  ratios above 1250 K.



#### 4.2.2 Oxidising system

The equilibrium distribution of As and Cr is not influenced by varying the  $Cl/C_{BC}$  ratio from 0.1 to 10. The volatile behaviour of Cd, Hg and Pb is not significantly altered under the same range of variations, but the chlorides  $CdCl_2$  (g),  $HgCl_2$  (g) and  $PbCl_2$  (g) decompose at higher temperatures when increasing the  $Cl/C_{BC}$  ratio. Meaning that only the gas phase chemistry is affected. For Cd a very small amount ( $< 3.5\%$  (mol/mol)) of  $CdO.SiO_2$  (cr) is observed at 950 to 970 K at a  $Cl/C_{BC}$  ratio of 0.1. The volatile behaviour of Cu, Ni and Zn is highly dependent on the  $Cl/C_{BC}$  ratio.

Insignificant influence when varying the  $Cl/C_{BC}$  ratio from 1.0 to 10 on the volatile behaviour of Cu is observed, meaning that Cu only is present in gas phase. However, at lower ratios the species  $CuO$  (cr) becomes more and more dominant in the lower temperature range. At a  $Cl/C_{BC}$  ratio of 0.1,  $CuO$  (cr) is the dominant species up to 1250 K. At 1300 K, Cu is only stable in the gas phase.

Ni shifts from being stable as  $2NiO.SiO_2$  (cr) over the entire temperature range at a  $Cl/C_{BC}$  ratio of 0.1 to being almost fully volatilised, at a  $Cl/C_{BC}$  ratio of 10, with  $2NiO.SiO_2$  (cr) only being present from 950 to 1030 K (decreasing from 67 to 0% (mol/mol)). Increasing the  $Cl/C_{BC}$  ratio, decompose  $2NiO.SiO_2$  (cr) at lower temperatures and increase the amount of  $NiCl_2$  (g).

Zn shows a volatile behaviour similar to Ni, when varying the  $Cl/C_{BC}$  ratio. With the exception of the presence of  $Zn$  (g) (less than 30% (mol/mol)) above 1450 K, Zn is stable as  $2ZnO.SiO_2$  (cr) over the entire temperature range at a  $Cl/C_{BC}$  ratio of 0.1. Increasing the  $Cl/C_{BC}$  ratio makes the presence of  $ZnCl_2$  (g) more and more dominating. Zn is only present in gas phase at a  $Cl/C_{BC}$  ratio of 10, with  $ZnCl_2$  (g) as the stable phase over the entire temperature range.

### 4.3 Effects of varying the air/fuel ratio ( $\lambda$ )

The equilibrium distribution of the different heavy metals was not largely altered, varying  $\lambda$  from 1.2 to 1.9 for the oxidising system. The volatility of Cd, Hg, Ni and Pb was not changed at all, while the observed effects on the other heavy metals are different from metal to metal. Zn becomes less volatile when increasing  $\lambda$ . At  $\lambda=1.2$  and a temperature of 1600 K, there is 22% (mol/mol) of  $2\text{ZnO}\cdot\text{SiO}_2$  (cr) in the system, while at  $\lambda=1.9$  this has increased to 71% (mol/mol) on the expense of Zn (g). The decreasing volatility of Zn is only observed in the higher temperature range, above 1450 K. The effect on the volatility of Zn in a real combustion plant would be enhanced since lowering  $\lambda$  also will increase the combustion temperature. Given the possibility of forming highly corrosive condensed zinc chlorides in the flue gas it is preferable to have Zn bound as  $2\text{ZnO}\cdot\text{SiO}_2$  (cr) in the bottom ash. At  $\lambda=1.9$  a part of Cu is present in solid phase as CuO (cr) (decreasing from 50 to 0% (mol/mol) from 950 to 1010 K). This is the only significant effect on the volatile behaviour of Cu when increasing  $\lambda$ . Cr becomes more volatile as the amount of gaseous chromium oxides increases with increasing  $\lambda$ . At 1600 K the amount of  $\text{CaO}\cdot\text{Cr}_2\text{O}_3$  (cr) gradually decreases from 96% (mol/mol) at  $\lambda=1.2$  to 71% at  $\lambda=1.9$ . For As the major effect of an increase in  $\lambda$  from 1.2 to 1.9 is that the equilibrium distribution has been shifted 70 K to a higher temperature. Meaning that an increasing in  $\lambda$  makes As slightly less volatile.

At reducing conditions, when varying  $\lambda$  from 0 to 0.9, the volatile behaviour of As, Cd, Cr, Hg and Pb are not significantly changed. Ni becomes slightly more volatile at temperatures above 1400 K, when increasing  $\lambda$ , due to the decomposition of Ni (cr,l) to  $\text{NiCl}_x$  (g) and Ni (g). The equilibrium distribution also becomes more complex at  $\lambda=0.9$  as compared to  $\lambda=0$ , with the presence of  $\text{Ni}_3\text{S}_2$  (cr,l) between 1150 and 1300 K and Ni chlorides at higher temperatures. Cu and Zn become less volatile with increasing  $\lambda$ . At  $\lambda =$

0, Cu and Zn is fully volatilised at 1350 and 1000 K, respectively, while the corresponding temperatures at  $\lambda=0.9$  are 1550 and 1150 K.

## 5. CONCLUSIONS

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 chemistry and devolatilisation behaviour of these metals has been studied using equilibrium calculations. Ash species have been included in order to investigate possible interactions with the heavy metals. These heavy metals behaves differently with respect to the volatility at combustion conditions in a 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.

The equilibrium calculations investigating the volatile behaviour on the grate shows that Cd, Hg and Pb is fully volatilised between 950 and 1600 K. Cr, however, is stable in solid phase practically over the entire temperature range. Only a small amount is volatilised at high temperatures. No influence on the volatility of Cr was observed when changing the sulphur or chlorine content. Cd, Hg and Pb showed no response, while Cr became slightly more volatile at higher temperatures with decreasing air/fuel ratio.

The volatile behaviour of As, Cu and Zn is largely altered when shifting from reducing to oxidising conditions. Whereas As and Zn become less volatile when shifting from reducing to oxidising conditions, Cu becomes more volatile. Changing the sulphur content only resulted in a change for Cu, making it less volatile with increasing sulphur content at reducing conditions.

At reducing conditions the volatile behaviour of As and Zn is not influenced by changes in the chlorine content, while Cu become more volatile when increasing the

content of chlorine. At oxidising conditions, Cu (at low chlorine content) and Zn become more volatile, while As experienced no change when increasing the chlorine content.

Although the equilibrium distribution changed, Ni experienced no change in the volatile behaviour when varying the sulphur content. Ni did, however, become more volatile when increasing the chlorine content, while varying  $\lambda$  did not significantly alter the volatile behaviour of Ni. These observations apply both for reducing and oxidising conditions.

Knowledge on the behaviour of heavy metals as they go from the furnace, being cooled through the boiler and end up in the flue gas cleaning system is also very important and will be focused upon in part II of this work.

## APPENDIX

### Species used in calculations

**Table 1.** Combustion products species used for both reducing and oxidising conditions. All species have thermodynamic data valid up to 2000 K.

| Combustion Products |                      |                                    |                                   |                     |
|---------------------|----------------------|------------------------------------|-----------------------------------|---------------------|
| CH <sub>4</sub> (g) | HCN (g)              | H <sub>2</sub> S (g)               | NOCl (g)                          | OH (g)              |
| CO (g)              | HCl (g)              | H <sub>2</sub> S <sub>2</sub> (g)  | NO <sub>2</sub> (g)               | O <sub>2</sub> (g)  |
| CO <sub>2</sub> (g) | HNO (g)              | H <sub>2</sub> SO <sub>4</sub> (g) | NO <sub>2</sub> Cl (g)            | S (g)               |
| COS (g)             | HNO <sub>3</sub> (g) | NH (g)                             | N <sub>2</sub> (g)                | SO (g)              |
| Cl (g)              | HS (g)               | NH <sub>2</sub> (g)                | N <sub>2</sub> H <sub>4</sub> (g) | SO <sub>2</sub> (g) |
| ClO (g)             | H <sub>2</sub> (g)   | NH <sub>3</sub> (g)                | N <sub>2</sub> O (g)              | SO <sub>3</sub> (g) |
| Cl <sub>2</sub> (g) | H <sub>2</sub> O (g) | NO (g)                             | O (g)                             | C (cr)*             |

\* Only included in calculations on reducing system.

**Table 2.** Ash species. All ash species have thermodynamic data valid up to 2000 K.

| Aluminium                                 | Silicon                                  | Calcium                             | Iron  |
|---|--|-------------------------------------|---|
| <b>Al (g)</b>                             | <b>Si (g)</b>                            | <b>Ca (g)</b>                       | <b>Fe (g)</b>   |
| <b>AlCl (g)</b>                           | <b>SiCl (g)</b>                          | <b>CaCl (g)</b>                     | <b>FeCl (g)</b>   |
| <b>AlCl<sub>2</sub> (g)</b>               | <b>SiCl<sub>2</sub> (g)</b>              | <b>CaCl<sub>2</sub> (g)</b>         | <b>FeCl<sub>2</sub> (g)</b>                             |
| <b>AlCl<sub>3</sub> (g)</b>               | <b>SiCl<sub>2</sub>H<sub>2</sub> (g)</b> | <b>CaO (g)</b>                      | <b>FeCl<sub>3</sub> (g)</b>                             |
| <b>AlO (g)</b>                            | <b>SiCl<sub>3</sub> (g)</b>              | <b>Ca(OH) (g)</b>                   | <b>FeO (g)</b>  |
| <b>Al(OH) (g)</b>                         | <b>SiCl<sub>4</sub> (g)</b>              | <b>Ca(OH)<sub>2</sub> (g)</b>       | <b>Fe(OH)<sub>2</sub> (g)</b>                           |
| <b>AlO<sub>2</sub> (g)</b>                | <b>SiH (g)</b>                           | <b>CaS (g)</b>                      | FeS (g)   |
| <b>AlS (g)</b>                            | <b>SiH<sub>4</sub> (g)</b>               | <i>Ca<sub>2</sub> (g)</i>           | Fe <sub>2</sub> Cl <sub>4</sub> (g)                     |
| <b>OAlCl (g)</b>                          | <b>SiO (g)</b>                           | CaCl <sub>2</sub> (cr) <sup>b</sup> | FeO (cr)  |
| OAl(OH) (g)                               | <b>SiO<sub>2</sub> (g)</b>               | CaCl <sub>2</sub> (l) <sup>b</sup>  | FeO (l) <sup>b</sup>                                    |
| <b>Al<sub>2</sub> (g)</b>                 | <b>Si<sub>2</sub> (g)</b>                | CaO (cr)                            | FeS <sub>0.877</sub> (cr) <sup>b</sup>                  |
| <b>Al<sub>2</sub>Cl<sub>6</sub> (g)</b>   | <b>Si<sub>3</sub> (g)</b>                | CaO (l)                             | <i>Fe<sub>2</sub>O<sub>3</sub> (cr)</i>                 |
| <b>Al<sub>2</sub>O (g)</b>                | <b>SiO<sub>2</sub> (cr,l)</b>            | <i>CaO (cr,l)</i>                   | <i>Fe<sub>3</sub>O<sub>4</sub> (cr)</i>                 |
| <b>Al<sub>2</sub>O<sub>2</sub> (g)</b>    |  | CaS (cr)                            | <b>FeO.Cr<sub>2</sub>O<sub>3</sub> (cr)<sup>a</sup></b> |
| <b>Al<sub>2</sub>O<sub>3</sub> (cr,l)</b> |  | <i>CaSO<sub>4</sub> (cr)</i>        |   |

**Bold:** Species used for both reducing and oxidising conditions.

Normal: Species used only for reduced conditions.

*Italic:* species used only for oxidising conditions.

<sup>a</sup> Only used in calculations with Cr.

<sup>b</sup> Used up to 1200 K.

**Table 3.** Heavy metal species used in calculations. The temperature indicates the maximum temperature for which the thermodynamic data are valid.

| Species   | Temperature | Species   | Temperature |
|---|-------------|---|-------------|
| <b>As (g)</b>   | 2000        | <b>Cr(OH)<sub>5</sub> (g)</b>   | 3000        |
| <b>AsCl<sub>3</sub> (g)</b>                           | 2000        | <b>CrO<sub>2</sub>(OH)<sub>2</sub> (g)</b>  | 3000        |
| AsH <sub>3</sub> (g)                                  | 2000        | <b>CrO(OH)<sub>4</sub> (g)</b>  | 3000        |
| <b>AsO (g)</b>  | 2000        | <b>Cr(OH)<sub>6</sub> (g)</b>   | 3000        |
| AsS (g)   | 1500        | CrS (g)   | 2000        |
| <b>As<sub>2</sub> (g)</b>                             | 2000        | Cr (cr)   | 2000        |
| As <sub>3</sub> (g)                                   | 2000        | <b>CrCl<sub>2</sub> (cr,l)</b>  | 1500        |
| As <sub>4</sub> (g)                                   | 2000        | CrCl <sub>3</sub> (cr)  | 1000        |
| As <sub>4</sub> O <sub>6</sub> (g)                    | 2000        | <b>Cr<sub>2</sub>O<sub>3</sub> (cr)</b>   | 2000        |
| As <sub>2</sub> O <sub>3</sub> (cr,l)                 | 700         | CrS (cr)  | 2000        |
| As <sub>2</sub> O <sub>5</sub> (cr)                   | 1000        | <b>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (cr)</b>  | 780/1000    |
| Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (cr) | 1700        | [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .2H <sub>2</sub> O (cr) | 540         |
|   |             | [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .3H <sub>2</sub> O (cr) | 540         |
|   |             | [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .4H <sub>2</sub> O (cr) | 540         |
|   |             | [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .5H <sub>2</sub> O (cr) | 540         |
|   |             | [Cr <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (SO <sub>4</sub> ) <sub>3</sub> ].2H <sub>2</sub> O (cr) | 540         |
| <b>Cd (g)</b>   | 2000        | <b>CaO.Cr<sub>2</sub>O<sub>3</sub> (cr)</b>   | 1900        |
| <b>CdCl<sub>2</sub> (g)</b>                           | 2000        |   |             |
| <b>CdO (g)</b>  | 2000        | <b>Cu (g)</b>   | 2000        |
| CdS (g)   | 2000        | <b>CuCl (g)</b>   | 2000        |
| Cd (cr,l)   | 1000        | <b>CuH (g)</b>  | 2000        |
| <b>CdCl<sub>2</sub> (cr,l)</b>                        | 1200        | <b>CuO (g)</b>  | 2000        |
| <b>CdO (cr)</b>                                       | 1700 /1200  | CuS (g)   | 2000        |
| <b>CdO.Al<sub>2</sub>O<sub>3</sub> (cr)</b>           | 1200        | <b>Cu<sub>2</sub> (g)</b>   | 2000        |
| <b>CdO.SiO<sub>2</sub> (cr)</b>                       | 1700 /1200  | <b>(CuCl)<sub>3</sub> (g)</b>   | 2000        |
| <b>Cd(OH)<sub>2</sub> (cr)</b>                        | 1200        | <b>CuCl (cr,l)</b>  | 1400        |
| CdS (cr)  | 1700/1200   | <b>CuO (cr)</b>   | 1300        |
| <b>CdSO<sub>4</sub> (cr)</b>                          | 1300/1200   | CuO.Al <sub>2</sub> O <sub>3</sub> (cr)   | 1400        |
|   |             | CuO.Fe <sub>2</sub> O <sub>3</sub> (cr)   | 1300        |
| <b>Cr (g)</b>   | 2000        | <b>CuS.FeS (cr)</b>   | 1200        |
| <b>CrCl<sub>2</sub> (g)</b>                           | 2000        | <b>CuSO<sub>4</sub> (cr)</b>  | 1000        |
| <b>CrCl<sub>2</sub>O<sub>2</sub> (g)</b>              | 2000        | Cu <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> (cr)   | 1200        |
| <b>CrCl<sub>3</sub> (g)</b>                           | 2000        | Cu <sub>2</sub> O.Fe <sub>2</sub> O <sub>3</sub> (cr)   | 1600        |
| <b>CrCl<sub>4</sub> (g)</b>                           | 2000        | Cu <sub>2</sub> S (cr,l)  | 2000        |
| <b>CrO (g)</b>  | 2000        | <b>Cu<sub>5</sub>FeS<sub>4</sub> (cr)</b>   | 1200        |
| <b>Cr(OH) (g)</b>                                     | 3000        |   |             |
| <b>CrO<sub>2</sub> (g)</b>                            | 2000        |   |             |
| <b>Cr(OH)<sub>2</sub> (g)</b>                         | 3000        |   |             |
| <b>CrOOH (g)</b>                                      | 3000        |   |             |
| <b>CrO<sub>3</sub> (g)</b>                            | 2000        |   |             |
| <b>Cr(OH)<sub>3</sub> (g)</b>                         | 3000        |   |             |
| <b>CrO(OH)<sub>2</sub> (g)</b>                        | 3000        |   |             |
| <b>Cr(OH)<sub>4</sub> (g)</b>                         | 3000        |   |             |
| <b>CrO<sub>2</sub>OH (g)</b>                          | 3000        |   |             |
| <b>CrO(OH)<sub>3</sub> (g)</b>                        | 3000        |   |             |

**Table 3. Continued.**

| Species                                     | Temperature | Species                                 | Temperature |
|---|-------------|---|-------------|
| <b>Hg (g)</b>                               | 2000        | <b>Pb (g)</b>                           | 2000        |
| <b>HgCl (g)</b>                             | 2000        | <b>PbCl (g)</b>                         | 2000        |
| <b>HgCl<sub>2</sub> (g)</b>                 | 2000        | <b>PbCl<sub>2</sub> (g)</b>             | 2000        |
| HgH (g)                                     | 2000        | <b>PbO (g)</b>                          | 2000        |
| <b>HgO (g)</b>                              | 2000        | PbS (g)                                 | 2000        |
| HgS (g)                                     | 2000        | <b>Pb<sub>2</sub> (g)</b>               | 2000        |
| <b>HgCl<sub>2</sub> (cr,l)</b>              | 1500        | Pb (l)                                  | 2000        |
| <i>HgO (cr)</i>                             | 1000        | <b>PbCl<sub>2</sub> (cr,l)</b>          | 2000        |
| <b>Hg<sub>2</sub>Cl<sub>2</sub> (cr)</b>    | 1500        | <b>PbO (cr,l)</b>                       | 2000        |
|   |             | <b>PbO.SiO<sub>2</sub> (cr)</b>         | 1800        |
| <b>Ni (g)</b>                               | 2000        | <b>2PbO.SiO<sub>2</sub> (cr)</b>        | 1800        |
| <b>Ni(CO)<sub>4</sub> (g)</b>               | 2000        | PbS (cr)                                | 1800        |
| <b>NiCl (g)</b>                             | 2000        | <b>PbSO<sub>4</sub> (cr,l)</b>          | 1800        |
| <b>NiCl<sub>2</sub> (g)</b>                 | 2000        | <b>Pb<sub>3</sub>O<sub>4</sub> (cr)</b> | 1500        |
| <b>NiO (g)</b>                              | 2000        |   |             |
| Ni (cr,l)                                   | 2000        | <b>Zn (g)</b>                           | 2000        |
| <b>NiCl<sub>2</sub> (cr,l)</b>              | 1400        | <b>ZnCl<sub>2</sub> (g)</b>             | 2000        |
| <b>NiO (cr)</b>                             | 2000        | ZnS (g)                                 | 2000        |
| NiO.Al <sub>2</sub> O <sub>3</sub> (cr)     | 2000        | Zn (cr,l)                               | 1100        |
| NiS (cr,l)                                  | 2000        | <i>ZnCl<sub>2</sub> (cr,l)</i>          | 900         |
| NiS <sub>2</sub> (cr,l)                     | 2000        | <b>ZnO (cr)</b>                         | 2000        |
| <b>NiSO<sub>4</sub> (cr)</b>                | 1200        | <b>ZnO.SiO<sub>2</sub> (cr)</b>         | 2000        |
| <b>NiO.Fe<sub>2</sub>O<sub>3</sub> (cr)</b> | 1500        | ZnS (cr,S)                              | 1300        |
| <b>2NiO.SiO<sub>2</sub> (cr)</b>            | 1800        | <b>ZnSO<sub>4</sub> (cr)</b>            | 1500        |
| Ni <sub>3</sub> S <sub>2</sub> (cr,l)       | 2000        | <b>2ZnO.SiO<sub>2</sub> (cr)</b>        | 2000        |
|   |             | <b>ZnO.2ZnSO<sub>4</sub> (cr)</b>       | 1200        |

**Bold:** Species used for both reducing and oxidising conditions.

Normal: Species used only for reducing conditions.

*Italic:* species used only for oxidising conditions.

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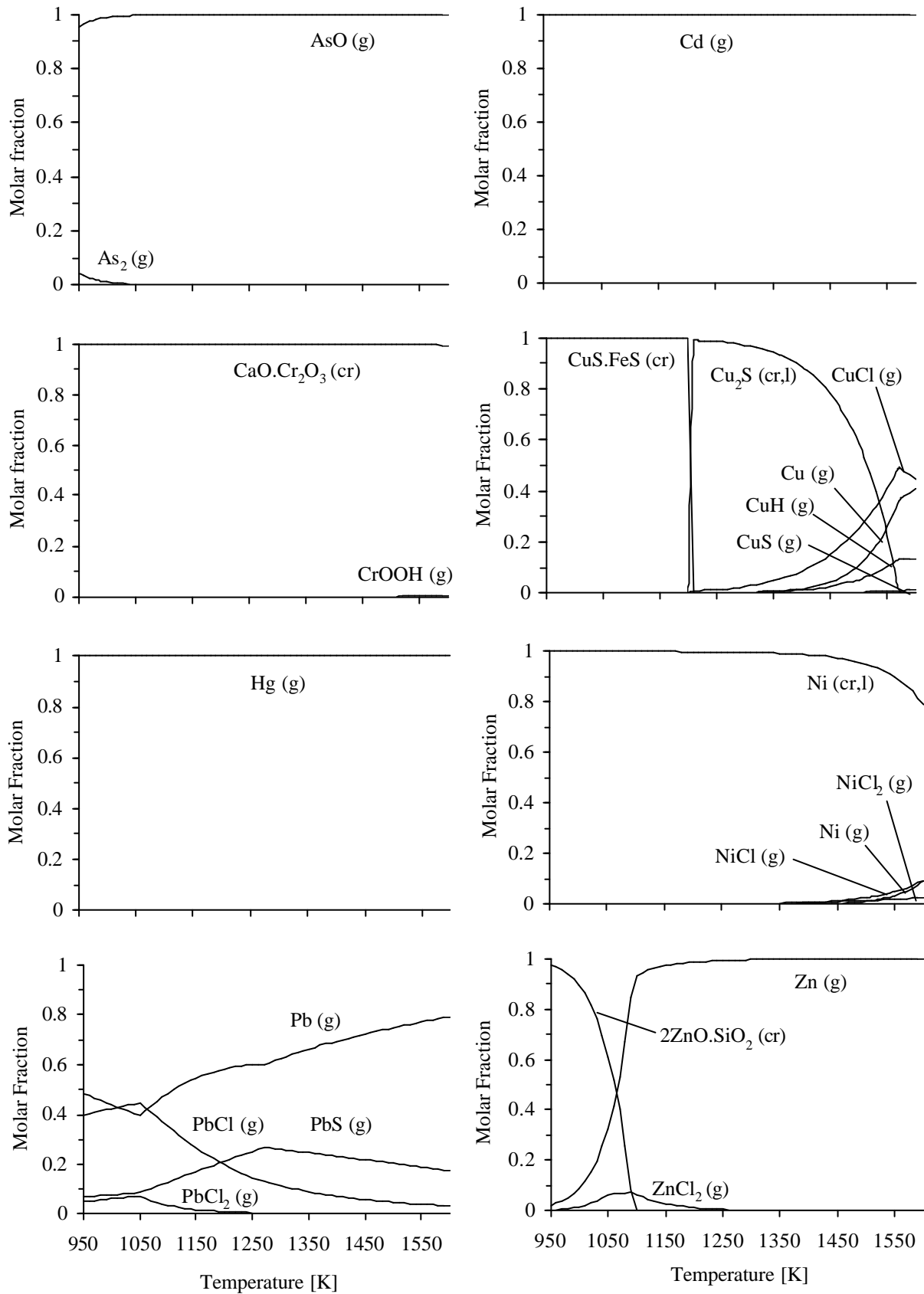
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**Table 4.** Ultimate analysis of base case composition for MSW.

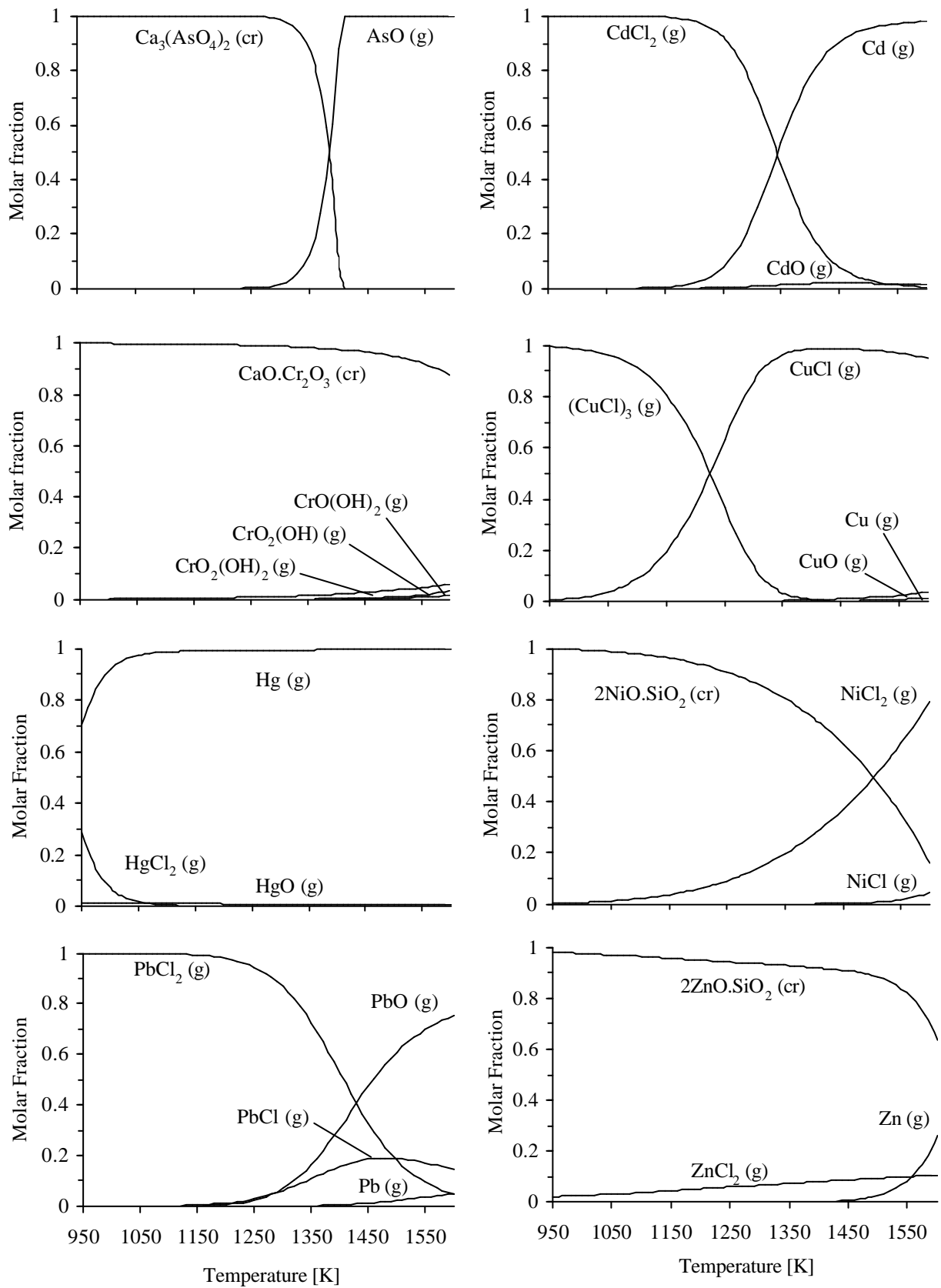
| Major species | Composition [wt%] | Trace elements | Concentration [g/ton] |
|---------------|-------------------|----------------|-----------------------|
| C             | 25.29             | As             | 18.2                  |
| H             | 3.39              | Cd             | 40.9                  |
| O             | 18.06             | Cr             | 55.7                  |
| N             | 0.48              | Cu             | 462.9                 |
| S             | 0.17              | Hg             | 1.1                   |
| Cl            | 0.56              | Ni             | 28.4                  |
| Moisture      | 24.82             | Pb             | 136.0                 |
| Ash           | 27.24             | Zn             | 1713.7                |

**Table 5.** Elemental composition of fuel and oxidiser for “ base case” calculations.

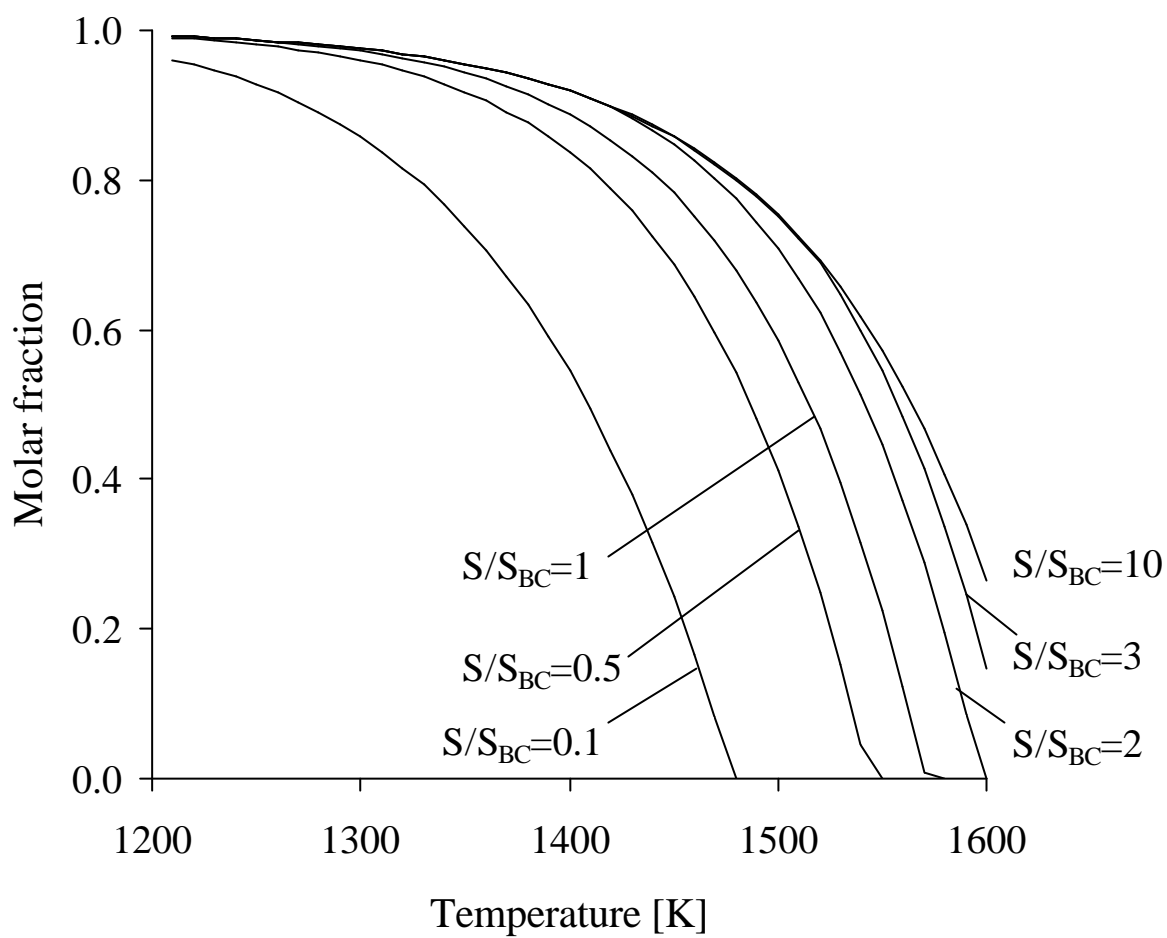
| Input parameters | Reducing conditions   | Oxidising conditions  |
|------------------|-----------------------|-----------------------|
| C [mole]         | 21.1                  | 21.1                  |
| H [mole]         | 61.5                  | 61.5                  |
| O [mole]         | 53.8                  | 85.5                  |
| N [mole]         | 108.3                 | 227.9                 |
| S [mole]         | 0.05                  | 0.05                  |
| Cl [mole]        | 0.16                  | 0.16                  |
| l                | 0.6                   | 1.3                   |
| Ash [wt%]        | 27.2                  | 27.2                  |
| Temp. [K]        | 950-1250              | 950-1250              |
| Al [mole]        | 0.234                 | 0.234                 |
| Ca [mole]        | 3.426                 | 3.426                 |
| Fe [mole]        | 2.153                 | 2.153                 |
| Si [mole]        | 0.300                 | 0.300                 |
| As [mole]        | $2.430 \cdot 10^{-4}$ | $2.430 \cdot 10^{-4}$ |
| Cd [mole]        | $3.637 \cdot 10^{-4}$ | $3.637 \cdot 10^{-4}$ |
| Cr [mole]        | $1.072 \cdot 10^{-3}$ | $1.072 \cdot 10^{-3}$ |
| Cu [mole]        | $7.290 \cdot 10^{-3}$ | $7.290 \cdot 10^{-3}$ |
| Hg [mole]        | $5.615 \cdot 10^{-6}$ | $5.615 \cdot 10^{-6}$ |
| Ni [mole]        | $4.843 \cdot 10^{-4}$ | $4.843 \cdot 10^{-4}$ |
| Pb [mole]        | $6.565 \cdot 10^{-4}$ | $6.565 \cdot 10^{-4}$ |
| Zn [mole]        | $2.620 \cdot 10^{-2}$ | $2.620 \cdot 10^{-2}$ |



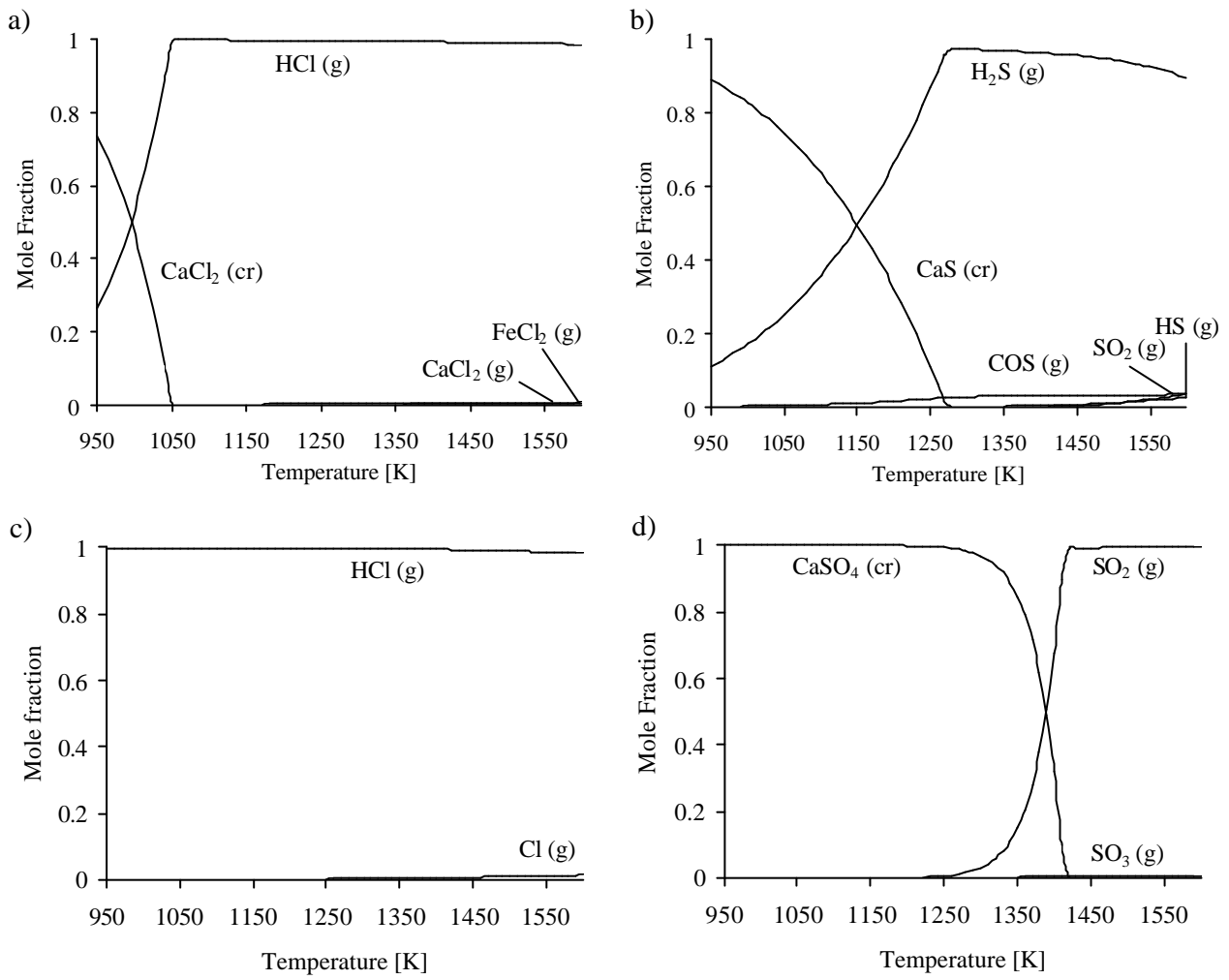
**Figure 1.** Equilibrium distribution of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn at reducing conditions on the grate.  $\lambda = 0.6$ .



**Figure 2.** Equilibrium distribution of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn at oxidising conditions on the grate.  $\lambda = 1.3$ .



**Figure 3.** Influence of the  $S/S_{BC}$  ratio on the volatility of  $Cu_2S$  (cr,l) as a function of temperature.



**Figure 4.** Chlorine and sulphur balances for the two different base case calculations. a) and b): reducing conditions on grate, c) and d): oxidising conditions on grate.