Fate of Cu, Cr, As and some other trace elements during combustion of recovered waste fuels

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by

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The increased use of biomass and recovered waste fuels in favor of fossil fuels for heat and power production is an important step towards a sustainable future. Combustion of waste fuels also offers several advantages over traditional landfiling, such as substantial volume reduction, detoxification of pathological wastes, and reduction of toxic leaches and greenhouse gas (methane) formation from landfills. However, combustion of recovered waste fuels emits more harmful trace elements than combustion of other fuels. These elements are distributed between bottom ash, fly ash and flue gas, depending on the elements partitioning and enrichment behavior. Volatilized harmful trace elements are mainly enriched in the submicron fly ash fraction. If emitted to the atmosphere, submicron particles can penetrate deep into the alveoli of the lungs, causing severe impacts on human health. Consequently, to reduce ash related problems and to control the emissions to the atmosphere, there is an increased need for understanding the physicochemical processes involved in ash transformation, including particle formation.

The objective of this thesis was to carefully and systematically study the fate of trace elements during combustion, i.e. the chemical form of the elements and the partitioning behavior, by means of chemical equilibrium model calculations, X-ray diffraction, microscopy techniques and various spectroscopy methods. The influence of some fuel additives was also analyzed. Primarily, the elements copper, chromium and arsenic were studied.

An initial review and evaluation of the content of thermodynamical data in commercial thermochemical databases used for chemical equilibrium model calculations showed that there was a significant difference in number of included phases and species between databases. Thermodynamical data also differed between databases, although in general less for condensed phases than for gaseous species. A state-of-the-art database for Cu, Cr and As was compiled and used for further chemical equilibrium model calculations. The fate of Cu, Cr and As was determined in combustion experiments on wood impregnated with copper, chromium and arsenic (CCA) in a bench scale reactor (15 kW). The results showed that global chemical equilibrium model calculations predicted the overall fate of Cu, Cr and As in bottom ash and ash particles quite well. However, compared to the experimental results the global model overpredicted the formation of refractory calcium arsenates, thus the arsenic volatilization was found to be higher then the predicted volatilization. In terms of chromium volatility, copper was found to be an important refractory element forming stable CuCrO$_2$(s) and CuCr$_2$O$_4$(s) that suppressed the formation of CrO$_2$(OH)$_2$(g). The retention and speciation of Cu, Cr and As in bottom ash was further determined from combustion experiments of CCA wood fuel particles in a single particle reactor. Local chemical equilibrium model calculations were performed to simulate the combustion stages of a burning CCA treated wood fuel particle: drying, devolatilization, char burning and post-combustion. The results from the work showed that a mix of local and global chemical equilibrium model calculations is needed to describe the reality and that the combustion stages are partially overlapping. The fate of harmful trace elements, including Cu, Cr and As, was finally studied in full scale (65 MW) combustion experiments. Particles from the raw flue gas emissions were sampled and analyzed. The comparison with chemical equilibrium model calculations showed that the model explained the results well, but due to lack of thermodynamic data for K$_2$ZnCl$_4$(s), the formation of this phase could not be predicted.

KEYWORDS: combustion, chemical equilibrium model calculations, trace elements, impregnated wood, waste, thermodynamic data, Cu, Cr, As
Syftet med denna avhandling är att bestämma var och i vilken kemisk form koppar, krom, arsenik och några andra hälso- och miljöstörande spårelement hamnar vid förbränning av sopor och sorterat rivningsvirke. Om spårelementen hamnar i bottenaskan återfinns de som fasta ämnen, vanligtvis som oxidier, sulfater, klorider, hydroxider eller karbonater, som alla är olika stabila och i varierande grad vattenlösliga. Spårelementen kan även bilda gasformiga föreningar som kan ombildas till fasta partiklar vilka därmed benämns som flygaska. Partiklarna i flygaskan varierar i storlek från ca 0.01 µm till 10 µm.

Förbränning av sopor är idag vanligt eftersom det både minskar sopberget och ger energi i form av värme och elektricitet. Andra fördelar med sopförbränning är att det bidrar till att minska de problem som finns med deponier i form av bildning av växthusgasen metan och utlakning av giftiga ämnen till grundvattnet. Det finns tyvärr en nackdel med sopförbränning och detta är att sopor innehåller mer tungmetaller och andra hälso- och miljöstörande spårelement än andra bränslen och dessa kan följa med rökgaserna ut genom skorstenen. Spårelementen som i högre grad ”kokas av” i gasfas anriktas oftast på de mindre partiklarna (<1 µm), som även är de svåraste för rökgasreningen att rena bort. Dessa kan vid inandning transporteras långt ner i lungorna där de kommer i nära kontakt med blodkärlen och därmed vidare in i kroppen.


Inledningsvis gjordes en sammanställning av de termodynamiska data som finns i de databaser som används för de kemiska jämviktsberäkningarna. Därefter sammanställdes en databas med bästa tillgängliga data för koppar-, krom- och arsenikföreningar som senare användes vid alla beräkningar. Olika förbränningsexperiment utfördes där tryckimpregnerat virke, innehållande koppar, krom och arsenik, eldades både som enskilda bränslepartiklar i en lab-skale anläggning vid Universitetet i Sydney, Australien och kontinuerligt i större mängd i en 15 kW anläggning vid Umeå Universitet. Askprover från bottenaska och rökgaser analyserades och resultatet jämfördes med kemiska jämviktsberäkningar. Resultatet visade att jämviktsberäkningarna överensstämde bra med det experimentella resultatet. De kemiska jämviktsberäkningarna utfördes både globalt och lokalt där de lokala beräkningarna simulerar förbränning av en enskild bränslepartikel. En jämförelse mellan de olika beräkningsmetoderna och det experimentella resultatet visade att verkligheten kan beskrivas som en blandning av globala och lokala jämviktsberäkningar och att förbränningsstegen torkning, pyroly, förbränning av pyrolysgaser samt koksförbränning delvis sker överlappande. Som sista delmoment togs prover på partiklarna i rökgaserna från en 65 MW sopförbränningsanläggning. En jämförelse mellan kemiska jämviktsberäkningar och resultaten från analyserna på askpartiklarna visade att beräkningarna förutsåg det experimentella resultatet från analyserna på askpartiklarna, men även att termodynamiska data saknas för en av huvudprodukterna (K₂ZnCl₄(s)).
Fate of Cu, Cr, As and some other trace elements during combustion of recovered waste fuels

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This thesis includes the following papers, in the text referred to by their Roman numerals I-V:

I Trace element speciation in combustion processes – Review and compilations of thermodynamic data
Karin Lundholm, Anders Nordin, Rainer Backman
Accepted for publication in Fuel Processing Technology

II Fate of Cu, Cr and As during combustion of impregnated wood with and without peat additive
Karin Lundholm, Dan Boström, Anders Nordin, Andrei Shchukarev
Accepted for publication in Environmental Science and Technology

III Fate of Cu, Cr and As during the combustion stages of burning CCA treated wood fuel particles
Karin Lundholm, Joseph M Rogers, Brian S Haynes, Dan Boström, Anders Nordin
Manuscript

IV Trace element speciation in a 65 MW MSW fired combined heat and power plant
Karin Lundholm, Dan Boström, Anders Nordin
Manuscript

V Chromium volatility by formation of CrO₂(OH)₂(g)
Karin Lundholm, Rainer Backman, Anders Nordin
Manuscript
Education is not the filling of a pail, 
but the lighting of a fire

(WB Yeats)
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### Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated Copper Arsenate</td>
</tr>
<tr>
<td>CCP</td>
<td>Chromated Copper Phosphate</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Trivalent Chromium</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Hexavalent Chromium</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic Precipitators</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FACT</td>
<td>Facility for the Analysis of Chemical Thermodynamics</td>
</tr>
<tr>
<td>HSC</td>
<td>H=enthalpy, S=entropy, C=heat capacity</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma - Atomic Emission Spectrometry</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma - Mass Spectrometry</td>
</tr>
<tr>
<td>ICP-SFMS</td>
<td>Inductively Coupled Plasma – Sector Field Mass Spectrometry</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>ITD</td>
<td>Integrated Thermochemical Database</td>
</tr>
<tr>
<td>JANAF</td>
<td>Joint Army-Navy-Air Force</td>
</tr>
<tr>
<td>NOx</td>
<td>NO, NO2, N2O, N2O3, N2O4, N2O5</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>RWW</td>
<td>Recovered Waste Wood</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>Scanning Electron Microscopy – Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>SGTE</td>
<td>Scientific Group Thermodata Europe</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
1 Introduction

Biomass and biomass derived waste materials are considered a sustainable energy source that has significant potential for replacing fossil fuels. Due to the increased concern for global warming and other environmental and political aspects, energy producing companies in Sweden use biomass and waste materials to an increasing extent in favor of fossil fuels for heat and power production. Sweden utilizes, from an international point of view, a high share of renewable sources. However, the politics of energy today is not only of national concern. Seeking to secure and diversify its energy supply, the European Union (EU) is governing the demand towards a more controlled and environmentally sustainable consumption through state taxes and integration of the European markets of energy to promote research and technical development. This has led to a new EU Directive on the incineration of waste [1] that was adopted late in the year 2000. It regulates among other things the harmful waste incineration emissions of particles and of twelve toxic elements; Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V. Consequently, there is an increased interest in monitoring and understanding the physicochemical processes involved in ash transformation during combustion of solid fuels, including particle and aerosol formation. In addition, to be able to maintain a sustainable energy production, to reduce ash related problems and to control the emissions to the atmosphere, the use of additives and different co-combustion approaches have to be carefully investigated.

1.1 Waste for energy in perspective

The EU Landfill Directive [2] demands for decreased use of landfill as the final storage for municipal solid waste (MSW). Combustion of MSW offers a number of advantages over storage in landfills. The reduction of the volume is substantial and a typical waste incinerator produces 5-10 % bottom ash of the original waste volume (20-30 % by weight) [3]. The combustion process also detoxifies pathological wastes, combustible carcinogens, mutagens and teratogens. Other advantages are reduction of leachable wastes from the landfills, and thus avoiding potential for soil and groundwater contamination, as well as reduction of methane gas and the net contribution to global warming. There is also a significant reduction of long-term odors that might be emitted into the atmosphere surrounding the landfill. Finally, the recovered energy can be used for district heating and electric power, which contributes to securing the energy supply and to decrease the use of fossil fuels and thereby reduce the effects of global warming.

However, combustion of MSW can also potentially impact human health and the environment in a number of ways and the amount and characteristics of air pollutants, process wastewater and ashes from MSW combustion plants are therefore regulated. To decrease pollution and improve ash quality, active sorting of waste (e.g. batteries, metals and other products unsuitable for combustion) by the households is also important. For example, if all batteries are sorted out from the waste, the mercury load in the MSW could be reduced by 50 % [4].
MSW is a very heterogeneous fuel and the composition varies with seasons and community. However, an average composition of household waste in Sweden was determined by sampling of garbage in seven representative household areas. The result is shown in Figure 1. The waste mainly consists of food wastes and recyclable waste, i.e. paper, cardboard, plastics, glass and metals.

![Figure 1. Composition of MSW in Sweden [5]](image)

Besides MSW, about 3-3.5 million tons of recovered waste wood (RWW) are generated annually from construction, demolition, and industrial activities, [6]. In Sweden, 70-80 % of all construction and demolition waste wood is combusted in biofuel boilers, while 5-10 % is combusted in municipal waste incinerators [7]. The energy retrieved from RWW comprises about 4 % of the total district heating in Sweden [8]. RWW mainly originates from demolition, renovation waste, and other sources such as packaging material e.g. wood pallets, polyethylene, styrofoam and cardboard [6]. However, the frequent contamination of RWW may cause problems of both technical and environmental nature. The most important materials contributing to contamination are impregnated wood, surface-treated wood, plastic and galvanized fastening systems (i.e. screws, nails and bolts) and therefore the RWW contains significant amounts of arsenic, chromium, copper, zinc, lead and nickel [9, 10]. Impregnated wood is the major source for copper, chromium and arsenic, and surface-treated wood contributes in particular to contaminants of zinc and lead [9]. About 5 % of the waste wood streams are estimated to consist of preservative treated timber in Sweden [11]. However, imported RWW representing nearly 50 % of the total waste wood combusted in Swedish incinerators contains higher concentrations of lead, mercury and cadmium [8]. The pollution sources for mercury, cadmium and nickel in RWW are less well understood although several possible sources such as concrete, stainless steel and electrical products can be outlined [10].
During waste incineration, elements such as Al, Cu, Fe, Ti and Zn are found largely in the slag, while more volatile elements such as Cd, Pb, Sb, Se and Sn are volatilized in the combustion zone and nucleate or condense on fine particles [12, 13]. Furthermore, chlorination of elements such as As, Cd, Ni, Pb, Sb and Zn during combustion may greatly increase volatilization and thus the presence of these elements in fly ash and submicron particles [13]. Also, a higher calorific value of the fuel increases volatilization of Cd, Cu, Pb and Zn [12], most probably due to more intense combustion. A compilation of the concentrations of the twelve regulated metals [1] and of zinc, chlorine and sulfur in MSW is shown in Table 1.

Table 1. Concentrations of trace elements in municipal solid waste (MSW). Values are given in g/ton.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>4-22</td>
<td>20</td>
<td>10.5</td>
<td>10-40</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;3-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>22-96</td>
<td>-</td>
<td>232</td>
<td>100-450</td>
</tr>
<tr>
<td>Cu</td>
<td>79-877</td>
<td>1000</td>
<td>489</td>
<td>450-2500</td>
</tr>
<tr>
<td>Hg</td>
<td>1-4.4</td>
<td>5</td>
<td>4.1</td>
<td>2-7</td>
</tr>
<tr>
<td>Mn</td>
<td>50-200</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>9-90</td>
<td>100</td>
<td>84</td>
<td>50-200</td>
</tr>
<tr>
<td>Pb</td>
<td>100-500</td>
<td>2000</td>
<td>455</td>
<td>750-2500</td>
</tr>
<tr>
<td>Sb</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tl *</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V *</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>200-2500</td>
<td>3000</td>
<td>1878</td>
<td>900-3500</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>5000</td>
<td>7540</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>1000</td>
<td>2700-5000</td>
<td>-</td>
</tr>
</tbody>
</table>

* No data was found since these elements were not regulated before 2000.

1.2 Preservative treated wood

In Sweden, preservative treated wood is considered a hazardous waste since January 2002 and thermal destruction is only allowed in approved combustion/incineration plants. Today, there are seven approved plants in Sweden and during 2004 the incinerated preservative treated wood amounted to 197,000 tons, about 20% of which were imported from Denmark, Norway, Switzerland, the Netherlands, Germany and Italy. Besides this, another 407,650 tons of mixed hazardous waste including impregnated wood was incinerated. No impregnated treated wood was exported from Sweden. [17]

Separation of preservative treated wood from the mixed wood sources is a challenge. While industrial treated products, such as poles and railway ties, are more easily separated, the residential treated wood will need some sorting technique. Visual sorting based on the
green color is not very effective since the distinction between used impregnated wood and untreated wood becomes less with time, although this method can potentially reduce the amount of impregnated wood entering the waste streams by 15-20% [18]. For sorting of smaller amounts of wood, spraying with chemical stains, which color the treated wood, can be effective. However, for quantities more than a few tones per year, laser or X-ray system techniques are more suitable.

One of the more commonly used preservatives for wood before 1994 contains copper, chromium and arsenic salts and is known as chromated copper arsenate, CCA. During impregnation, the metal compounds in a CCA solution are fixed to the cell walls of the wood matrix. The fixation process of CCA to wood can be schematized as shown in Figure 2.

![Diagram of CCA interaction with wood](image)

Figure 2. Scheme of the interaction of CCA with wood [19].

A substantial amount of CCA remains in the wood for several years and thereby prevents microbial attacks. CCA treated wood are widely used, for example, in telephone poles, decks, fence posts, docks, and foundations. In Sweden, about 300 000 m³ of preservative-treated sawn timber is produced annually for the domestic market. The total annual use of CCA preservatives in Sweden between 1970 and 1995 amounted approximately to 290-, 225- and 220 tons of arsenic, copper and chromium, respectively [11]. The increased use of copper, chromium and arsenic from 1950 to 1990 are shown in Figure 3. Leaching of these elements from timber during the first year of use, due to exposure to moisture, is of great concern as there exists a potential for soil and groundwater contamination. Also the wearing of wood releases the toxic elements to nature. The loss of Cu, Cr and As by leaching and wearing can be accounted up to 15% [20]. However, new regulations for chromium- and arsenic preservatives in 1994 have decreased the use of CCA preservative wood from 80% market share to between 40 to 50% [11]. Despite new regulations, there is still a large amount of CCA-treated wood in use that will be replaced in the future and thereby end up as waste.
The wood preservatives that are replacing CCA are based on copper as the active component and boron, tebukonazol or benzalkonium chloride as a secondary active component [11]. These secondary components contain nitrogen and chlorine, which can be of further interest regarding NOx emissions and corrosion. Copper chromated phosphate (CCP) preservative is also more commonly used today, where arsenic is replaced by phosphorus.

1.3 Partitioning of trace elements

The most abundant elements in biomass fuels are C, H and O, which are called the “major” elements. “Minor” elements are present in lower amounts, but generally above 0.01 wt. % and include K, Mg, Ca and P. Trace elements are found in concentrations lower than 0.01 wt. % and include most metals [22] and arsenic. Metals have traditionally been classified into different categories such as light, heavy, metalloids, toxic and trace, all depending on their physical and chemical properties. Trace metals in natural media are present at concentrations less than 0.1 % whereas a heavy metal refers to metals with a density greater than 5.0 \( \mu \text{g m}^{-3} \) [23]. Most trace metals are associated with pollution and toxicity, although some of the elements are essential in lower concentrations.

During combustion, trace elements can be categorized depending on partitioning and enrichment behavior. Partitioning is referred to as the distribution among different emission streams. The partitioning of trace metals during combustion begins in the fuel particle and continues in the high temperature radiant section of the furnace. The trace elements are then distributed between bottom ash, fly ash and flue gas emissions, depending on the degree of volatilization and to which extent they are physically and chemically bound to the carbon matrix or minerals in the fuel. The volatility of metals is influenced by the waste composition (including metals and halogens), the combustion

![Figure 3. The use of copper, chromium and arsenic in the production of impregnated wood during the years 1950-1990 [21].](image-url)
temperature, and the air to fuel ratio [24]. Those elements that are not volatilized during combustion generally forms a melt as well as crystalline phases [25], whereas the vaporized components will cool through the post-furnace system. The fate of the vaporized components depends on their transformation into various solid forms and their absorption onto fly ash particles. Particle size distribution is dependent on the mechanism of formation of the particles. Fast chemical reactions may lead to supersaturated vapors and initiation of nucleation and thereby formation of very small particles from the vapor phase. Condensation forms larger particles when the vapor molecules collide or diffuse to the particle surface. The largest particles are formed by coagulation, which is a particle to particle collision process followed by adhesion [26]. Figure 4 shows the vaporized metal transformation process during combustion. The processes involved in partitioning are important for the choice of emission control device.

Figure 4. Formation of inorganic ash particles during combustion of solid fuels. Based on earlier versions [27-29]
According to Clarke and Sloss [25], metals can be classified into three basic groups depending on their partitioning and enrichment behavior during combustion of coal in a suspension reactor:

Group I. The least volatile elements which show no significant enrichment or depletion in the fly ash.
Group II. Semivolatile elements which are enriched in the fly ash and depleted in the bottom ash and show increasing enrichment with decreasing fly ash particle size.
Group III. Elements which are volatilized and concentrated in the vapor phase and not enriched in the residue streams.

The group assignment of an element could as a first estimate be predicted based on the boiling points of the element and its compounds and at which temperature phase transformation occurs. However, in many cases elements have intermediate behavior, which place them in more than one class. Figure 5 shows an overlapping classification of trace elements for combustion systems.

![Classification of trace elements based on behavior during combustion and gasification](image-url)

Particles from combustion have been shown to represent a bimodal particle mass size distribution in the micron and submicron range [28]. The definition of particle size is that coarse particles are greater than 1 µm and fine particles are less than 1 µm. Ultrafine particles are smaller than 0.1 µm. This can be compared with known biogenic allergens such as pollen, spores and proteins: Most pollen is larger than 10 µm, spores are typically 2-10 µm, bacteria are 0.5-20 µm, and viruses are less than 1 µm.

Studies of particle surface layers using spectroscopic methods have shown that the surface layers of both supermicron and submicron [30-33] ash particles are enriched in trace elements. However, submicron particles dominate the number count of particles from combustion and most toxic elements are enriched in the submicron fly ash fraction (such
as As, Cd, Cr, Pb, Hg, Ni, Se, Sb). This trend is not unambiguous though and Davison [33] for example found lead in significant concentrations in particles greater than 10 µm in diameter. It should also be pointed out that the presence of chlorine enhances the volatilization of most metals and thereby shifts the particles to a finer distribution i.e. the submicron fraction [13, 34].

The most effective electrostatic precipitators (ESP) and filters remove more than 99% of the fly ash particles, but a small proportion of mainly submicron particles are emitted to the atmosphere with the stack gases [35]. The collection efficiency of electrostatic precipitators for the submicron particles is less compared to that for ultrafine and coarse particles [28, 36-38]. Moreover, particles less than 1 µm have a greater impact on health since these particles can penetrate deep into the lungs where toxic metals would be in close contact with the blood supply. They can also stay airborne for long periods of time, which makes them a more significant problem of control than larger particles [33, 39]. Fabric filters are therefore a better alternative than ESP for the collection of submicron dust, and a fabric filter in combination with dry injection or a downstream scrubber increases the collection efficiency further [3]. Barton [40] found that the parameters that most affect the general metal emission trends and capture efficiency are: the incinerator temperature, the waste chlorine content, the metal type and the flue gas cleaning devices. However, the partition of metals between bottom ash and fly ash is more dependent on furnace design than operation conditions [41].

1.3.1 Copper

The partitioning behavior of copper during combustion or gasification classifies it as an intermediate element between group I and II, i.e. distributed mainly between both bottom ash and fly ash. The distribution of copper between bottom ash, fly ash and flue gas after combustion of different fuels is shown in Table 2.

Table 2. Distribution of copper in ash (wt. %).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Emission control</th>
<th>Bottom ash</th>
<th>Fly ash *</th>
<th>Flue gas</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood+Bark Filter</td>
<td>38-55</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>Wood+Bark Filter</td>
<td>61.9</td>
<td>34.3</td>
<td>3.7</td>
<td></td>
<td>Nardoslawsky et al. [43]</td>
</tr>
<tr>
<td>Sewage sludge Filter</td>
<td>19.3-55.2</td>
<td>44.6-80.6</td>
<td>0.2-0.8</td>
<td></td>
<td>Corella et al. [44]</td>
</tr>
<tr>
<td>Coal Filter</td>
<td>78-100</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>MSW Lime+Fabric filter</td>
<td>89</td>
<td>11</td>
<td>0</td>
<td></td>
<td>Terkildsen [45]</td>
</tr>
<tr>
<td>MSW ESP</td>
<td>89</td>
<td>10</td>
<td>1</td>
<td></td>
<td>Brunner et al. [12]</td>
</tr>
<tr>
<td>10 % CCA, 90 % MSW</td>
<td>Lime+Fabric filter</td>
<td>87</td>
<td>13</td>
<td>0</td>
<td>Terkildsen [45]</td>
</tr>
</tbody>
</table>

* Includes coarse fly ash, cyclone ash, and filter ash

Problems with copper in combustion processes not only involve toxic ashes, but also the fact that copper, especially in presence of chlorine, can catalyze the formation of highly toxic dioxins. Terkildsen [45] showed that dioxins in stack gases increased from 2.5 to 8.1 ng/nm³, while the concentration in fly ash increased from 240 to 2000 ng/kg when
wood impregnated with copper, chromium and phosphor were added to a waste fuel. Copper were believed to be the explanation for the results.

1.3.2 Chromium

The partitioning behavior of chromium, like copper, classifies as an intermediate element between group I and II. Chromium occurs in oxidation states ranging from divalent (II) to hexavalent (VI), where the trivalent and hexavalent states are commonly found in nature [46]. Trivalent chromium is an essential trace element for humans, whereas hexavalent chromium is considered carcinogenic and can cause lung cancer when it is inhaled as dust or fine particles [47]. The volatilization of chromium at high temperatures from both fuel sources [48, 49] and stainless steel [50-52] is thus an important issue: is the formed gaseous chromium, potentially involved in sequential aerosol and particle formation, hexavalent? Goodarzi [53] found that less than 5% of the chromium from coal was found as Cr(VI) in bottom ash and fly ash, although one sub-bituminous coal resulted in up to 20% of Cr(VI) in the fly ash. Seigneur and Constantinou [54] studied the kinetics and mechanism for the conversion of Cr(III) to Cr(VI) and vice versa and found that Cr(III) can be oxidized to Cr(VI) by reactions with manganese, and Cr(VI) can be reduced to Cr(III) by trivalent arsenic, divalent iron, vanadium and sulfur dioxide. Table 3 shows the distribution of total chromium after combustion of different fuels.

Table 3. Distribution of chromium in ash (wt. %).

<table>
<thead>
<tr>
<th>Fuel Emission control</th>
<th>Bottom ash</th>
<th>Fly ash *</th>
<th>Flue gas</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood+Bark Filter</td>
<td>75-77</td>
<td></td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>Wood+Bark Filter</td>
<td>72.6</td>
<td>25.6</td>
<td>1.8</td>
<td>Nardoslawsky [43]</td>
</tr>
<tr>
<td>Sewage sludge Filter</td>
<td>24.4</td>
<td>75.5</td>
<td>0.1</td>
<td>Corella et al. [44]</td>
</tr>
<tr>
<td>Coal Filter</td>
<td>50-95</td>
<td></td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>MSW Fabric filter</td>
<td>96</td>
<td>1</td>
<td>3</td>
<td>Thipse et al. [55]</td>
</tr>
<tr>
<td>MSW ESP</td>
<td>88</td>
<td>9</td>
<td>3</td>
<td>Wey et al. [34]</td>
</tr>
<tr>
<td>MSW Fabric filter</td>
<td>98</td>
<td>1</td>
<td>1</td>
<td>Binner et al. [56]</td>
</tr>
<tr>
<td>MSW Lime+Fabric filter</td>
<td>65</td>
<td>34</td>
<td>1</td>
<td>Terkildsen [45]</td>
</tr>
<tr>
<td>10% CCA, 90% MSW Lime+Fabric filter</td>
<td>62</td>
<td>38</td>
<td>0</td>
<td>Terkildsen [45]</td>
</tr>
</tbody>
</table>

* Includes coarse fly ash, cyclone ash, and filter ash

1.3.3 Arsenic

Arsenic volatilize already below typical combustion temperatures and As₂O₅ have been reported to volatilize at 600°C in air and already at 320°C during smoldering combustion of a sawdust/As₂O₅ mix [57]. During combustion, As₂O₅ transforms to As₅O₃, which vaporize at temperatures below the combustion temperature, see Reaction (1) and (2).

\[
\text{As}_2\text{O}_5 (s) \Rightarrow \text{As}_2\text{O}_3 (s) + \text{O}_2 (g) \quad 794.54 \text{ K} (p(H_2O)=0.21) \quad (1)
\]

\[
\text{As}_2\text{O}_3 (s) \Rightarrow \text{As}_2\text{O}_3 (g) \quad 408 \text{ K} [58] \quad (2)
\]
The partitioning behavior of arsenic is classified as a group II behavior (see above), i.e. arsenic is a semivolatile element enriched in the fly ash and depleted in the bottom ash, showing increasing enrichment with decreasing fly ash particle size. Results from partitioning analyses are shown in Table 4.

### Table 4. Distribution of arsenic ash (wt. %).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Emission control</th>
<th>Bottom ash</th>
<th>Fly ash</th>
<th>Flue gas</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood+Bark</td>
<td>Filter</td>
<td>24-42</td>
<td></td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>Wood+Bark</td>
<td>Filter</td>
<td>51.6</td>
<td>44.7</td>
<td>3.7</td>
<td>Nardoslawsky [43]</td>
</tr>
<tr>
<td>Coal</td>
<td>Filter</td>
<td>23-57</td>
<td></td>
<td></td>
<td>Miller et al. [42]</td>
</tr>
<tr>
<td>MSW</td>
<td>Lime+Fabric filter</td>
<td>25</td>
<td>75</td>
<td></td>
<td>Terkildsen [45]</td>
</tr>
<tr>
<td>CCA</td>
<td>Filters</td>
<td>23-72</td>
<td>27-77</td>
<td>32</td>
<td>McMahon [59]</td>
</tr>
<tr>
<td>CCA</td>
<td>-</td>
<td>32</td>
<td>26</td>
<td>32</td>
<td>Gifford [60]</td>
</tr>
<tr>
<td>CCA 10 % CCA,</td>
<td>Lime+Fabric filter</td>
<td>17</td>
<td>83</td>
<td></td>
<td>Terkildsen [45]</td>
</tr>
<tr>
<td>90 % MSW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Includes coarse fly ash, cyclone ash, and filter ash

However, partitioning is influenced by the amount of arsenic in the fuel and the fuel type. Gifford [60] showed that the amount of CCA-wood in the wood/bark fuel affected the relative distribution of arsenic between ash, particles and gas phase (see Figure 6). The vaporization of arsenic from coal varied between 55 to 99 %, with increased vaporization for higher coal ranks [61]. Also, the amount of available refractory elements such as calcium can significantly decrease the fraction of vaporized arsenic [62-65]. Therefore, depending on the combustion conditions, i.e. the fuel, the combustion temperature and the oxygen content of the combustion air [66], more or less of the arsenic in the waste stream ends up in the fly ash or flue gas emissions.

![Figure 6](image-url)  
**Figure 6.** Relative distribution of arsenic between ash, particulate phases and volatile gases with different amounts of CCA treated wood co-combusted with a fuel mixture of wood and bark. Arsenic emissions were below the sampling method detection limit for fuels comprised of less than 5 % of CCA wood.
However, experimental studies with CCA-wood often report mass balances of arsenic that are far below 100%. This deficiency can be due to incomplete sampling or that some of the volatilized $\text{As}_2\text{O}_3$ is precipitated in flue gas channels due to low sublimation temperature.

### 1.4 Objectives of the present work

The objective of the work included in this thesis was to carefully and systematically study the fate of trace elements during combustion with respect to formed phases and species, partitioning behavior and influences of fuel additives. Primarily, the elements copper, chromium and arsenic were studied during combustion of preservative treated wood. However, during combustion of MSW also lead, zinc and cadmium were studied.
2 Methods

The fate of copper, chromium, arsenic and some other trace elements was studied using different analysis methods. This was done to improve the understanding of the chemical processes occurring during combustion. X-ray diffraction, microscopy, various spectroscopy methods, and chemical equilibrium model calculations were used to examine the chemical speciation of the ash forming elements, their distribution in ash fractions and ash particle sizes, and to interpret different chemical reactions during combustion.

2.1 Chemical Equilibrium Model Calculations

Chemical equilibrium model calculations were generally used to help interpret the experimental findings. The modeling programs use the Gibbs free energy minimization approach, which is based upon two assumptions:

1. all elements are intimately mixed
2. all reactions achieve equilibrium

This approach makes it possible to perform complex chemical equilibrium calculations in multicomponent multiphase systems, which delineate the stable phases and dominating species that can form during specific operating conditions. The calculations can simulate the total combustion process (global equilibrium analysis) or local conditions (local equilibrium analysis), for example in a burning fuel particle or at a specific part of the reactor. The software program FactSage, together with thermodynamic data from the FACT database [67], the SGTE database [68], the HSC database [69], and data presented by Ebbinghaus [70, 71] and Rosén [72] was used for the calculations in paper II, III and IV. Thermodynamic data were also used from the IVTANTHERMO database [73] and calculated from experimental results from Gindorf et al. [74, 75] in paper V.

2.2 X-ray diffraction

The structure and identity of crystalline phases in ashes from combustion can be determined using powder X-ray diffraction analysis (XRD). The X-ray wavelength is of the same order of magnitude as the bond distances between atoms. As a result, the crystal array scatters the X-rays in a pattern that is unique for the particular atomic arrangement in a sample. Applied on combustion chemistry research on metals, XRD is a pertinent tool together with chemical equilibrium calculations for indication of different reactions during the processes of combustion. Also, small ash particle samples collected on impactor substrates (< 1 mg) can preferably be analyzed. Unfortunately, the identity of amorphous material can not be determined and its presence frequently causes diffuse features in the diffraction patterns. XRD was used in paper II, III, and IV for identification of crystalline phases in different ash fractions. The analyses were performed at Energy Technology and Thermal Process Chemistry (ETPC), Umeå University by associate professor Dan Boström in collaboration with the author of the thesis. A Bruker d8Advance instrument in θ-θ mode, with an optical configuration consisting of a primary Göbel mirror and a Väntec-1 detector was used. Continuous scans were applied on the sample that was mounted on a rotating low-background Si-single-crystal sample holder. By
adding repeated scans, the total data collection time for each sample lasted for at least 10 hours. The PDF2 databank [76] and the ICSD database [77] together with Bruker software was used to analyze the diffraction patterns.

### 2.3 Scanning electron microscopy with energy dispersive spectroscopy

To image the morphology, and also analyze the elemental composition of the ashes, scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS) was used. The application of “reflected” electrons instead of light, results in image resolutions in the nanometer scale. By detecting X-rays emitted from the sample during exposure to electrons, the elemental composition can also be determined. The emitted X-rays have characteristic energies, which are used to determine the elemental composition of the sample. However, when the X-rays have passed through the EDS system, the peaks of the spectrum have a width of ≥ 130 eV. The natural variation in energy between X-ray photons from a certain electron transition is about 2 eV. This decrease in energy resolution results in overlapping and lower peaks. Since low peaks may disappear in the background noise, the detection sensitivity for small concentrations of elements becomes somewhat reduced and ICP-SFMS (see below) was therefore used as a complement. A Philips model XL30 environmental scanning electron microscope (ESEM) equipped with an EDAX EDS was used in paper II, III and IV.

### 2.4 X-ray photoelectron spectroscopy

To determine and quantify the chemical composition of a sample surface, X-ray photoelectron spectroscopy (XPS) is preferably used. The X-rays striking the surface of the sample cause photoemission of electrons from the atoms. From the measured kinetic energy of the emitted electrons and the energy of the incident beam, the electron binding energy can be calculated. The binding energy for core level electrons is specific for each element and orbital and thereby it is possible to elucidate the elemental composition of a surface. It is also possible to distinguish between different oxidation states of an element, since the binding energy also is influenced by different oxidation states of an atom. The XPS analyses were performed at Inorganic Chemistry, Umeå University by associate professor Andrei Shchukarev. XPS spectra were recorded with a Kratos Axis Ultra electron spectrometer using a monochromated Al Kα source, a hybrid lens system with magnetic lens, and a charge neutralizer. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with Kratos software. The chemical states of As and Cr in particles from impactor samples was determined using XPS in paper III.

### 2.5 Inductively coupled plasma spectroscopy

To identify elements in fuels and ashes and to quantify the element concentrations, inductively coupled plasma spectroscopy methods were used. Inductively coupled plasma (ICP) is an electrically neutral, very high temperature excitation source, which constitutes of plasma containing a sufficient concentration of ions and electrons, which is produced by electromagnetic induction.
Inductively coupled plasma atomic emission spectrometry (ICP-AES) uses plasma to produce excited atoms that emit electromagnetic radiation at a wavelength characteristic of a particular element. The intensity of the emission is indicative of the concentration of the element. The detection limit is µg/L. ICP-AES was used in paper II and III.

Inductively coupled plasma mass spectrometry (ICP-MS) uses plasma to ionize the atoms of the elements. The ions are then separated by mass in a mass spectrometer, which allows for measurements of the mass-to-charge ratio of ions and hence the concentration. The detection limit is ng/L. ICP-MS was used in paper II.

Inductively coupled plasma sector field mass spectrometry (ICP-SFMS) differs from ICP-MS in the mass spectrometer. ICP-SFMS uses sector fields instead of a quadrupole to separate the ions, which can be used even at low resolutions and thereby achieve extremely low detection limits of pg/L for some elements. ICP-SFMS was used in paper IV.

These methods can separate between isotopes, but the methods are not able to distinguish between different oxidation states of an atom. The ICP spectroscopy analyses in paper II and V were performed by the ALS Laboratory group in Luleå, and the analyses in paper III at the department of Chemical Engineering, University of Sydney.
3 Thermochemical databases and thermodynamical data

As described previously, chemical equilibrium model calculations is a useful tool for interpretation of chemical processes, regarding the driving forces, fate and final products of different reactants. However, without reliable thermodynamic data, the results from the calculations are questionable. Knowledge of the quality of data in the different reference databases together with variation in content of trace element species and phases, is thus important. Therefore, a comparison and evaluation of thermodynamic data from three commercial thermochemical databases was initially performed in paper I. The selected databases were FACT [67], SGTE [68] and HSC [69]. The FACT database (Facility for the Analysis of Chemical Thermodynamics) that was initiated in Canada 1979 by Ecole Polytechnique de Montreal and McGill University in collaboration with THERMFACT INC. SGTE (Scientific Group Thermodata Europe) is a legally constituted consortium of centers, initially located in Europe, engaged in the development of thermodynamic data. HSC, which is a product by the Finnish Outokumpu Technology, is an abbreviation of enthalpy (H), entropy (S) and heat capacity (Cp). All three databases are Integrated Thermochemical Databases (ITD), which means that the database is in unison with powerful computational software. Complex chemical equilibrium calculations and phase diagram calculations in multicomponent multiphase systems can therefore be performed. The members of SGTE share the same thermodynamical data but the software programs are independently supported. Collaboration between THERMFACT/CRCT and GTT-Technologies (member of SGTE) has resulted in a software program (FactSage) that includes the FACT database and supports the SGTE database. Finally, as a reference, Thermochemical data of pure substances [78] were selected and uncertainties in absolute G-values were calculated using uncertainties for entropy and enthalpy from the tables of JANAF [79], as it is the major reference for Thermochemical data of pure substances.

The compounds studied were those containing the toxic elements As, Cd, Cr, Cu, and Pb together with C, O, H, N, S, Cl. However, metal-metal compounds were not considered. The results of the comparison showed that none of the three databases contained all possible phases and species available. The database with most compounds included was the HSC database. The FACT and the SGTE database are approximately equivalent in number of compounds included, but combining the two will make a database comparable with the HSC database. Comparing absolute G-values between databases showed significant differences, although in general smaller for condensed phases than for gaseous species. Also, the uncertainties in G-values were smaller for condensed phases than for the gaseous species.

However, small differences in thermodynamic data may still result in significant differences for the outcome of chemical equilibrium calculations. The results, when using different databases for the same equilibrium calculations for arsenic and cadmium are illustrated in Figure 7. For arsenic compounds, the difference in the results of chemical equilibrium calculations between the HSC and SGTE database was not significant, whereas the difference between the FACT database and the other databases was obvious. However, there was still a discrepancy of 50°C if the same number of compounds were allowed for all databases (see Figure 7, left, bottom), signifying not only differences in
number of included species but also differences in thermodynamic data. For cadmium, the small difference in thermodynamic data for CdO(s) and Cd(g) between the SGTE and HSC database resulted in small discrepancies. However, there was a large difference in thermodynamic data for CdO(g), CdOH(g) and Cd(OH)$_2$(g) between the Fact database and the other two databases, which resulted in large discrepancies above 900°C.

![Figure 7](image)

**Figure 7.** Equilibrium calculation results for the system As-C-O-H-N-Cl-S (left) and Cd-C-O-H-N (right) in a typical combustion atmosphere using different thermodynamic data. Results using the SGTE or the HSC database are shown in the upper figures, bottom figures shows results using the FACT database. In the bottom figure to the left, only the arsenic compounds available in the FACT database are used and compared with results obtained using the same compounds from the SGTE or the HSC database.

Chromium was the element with largest differences in number of included volatile species between the databases. Data for some of the chromium hydroxides, oxohydroxides chlorides and oxochlorides from the IVTANTHERMO database [73] has been adopted by the HSC and SGTE databases, but the full list from Ebbinghaus [70, 71] was not available in any database. In the latest FACT database update though (Jan 2006), the full list from Ebbinghaus is now included. Both Ebbinghaus and IVTANTHERMO data are based on ab initio calculations, however experimental data for the most prevalent gaseous hexavalent chromium specie formed in high temperatures, i.e. CrO$_2$(OH)$_2$(g), can be found from both Gindorf et al. [74, 75] and now recently from Opila et al. [80]. Thermodynamic data from the results of Gindorf et al. were estimated in paper V. The difference in data for CrO$_2$(OH)$_2$(g) between these sources are shown in Figure 8.
Figure 8. Vaporization of CrO$_2$(OH)$_2$(g) from Cr$_2$O$_3$(s) in air with constant humidity, $p$(H$_2$O$)=0.1$ bar. Thermodynamic data on CrO$_2$(OH)$_2$(g) was taken from Ebbinghaus, the IVTANTHERMO database, Gindorf et al. and Opila et al. Thermodynamic data on Cr$_2$O$_3$(s), O$_2$(g), and H$_2$O(g) were taken from the IVTANTHERMO database.

Data from both Gindorf et al. and Opila et al. report data indicating higher volatility than data from the IVTANTHERMO database but somewhat lower then suggested by Ebbinghaus. Preliminary direct measurements of CrO$_2$(OH)$_2$(s) by molecular mass beam spectrometry by Persson et al. [81] also support the significant formation and rather high volatility of CrO$_2$(OH)$_2$(s). Opila et al. suggested two reasons for the discrepancies between the results from the different sources: (i) the lower volatility of CrO$_2$(OH)$_2$(g) reported by Gindorf et al. was probably due to incomplete recovery of transported chromium, which was either left in the collected water or not completely removed from the condensation tubes of the high-temperature experiments; (ii) the narrow range of conditions in the experiments of Gindorf et al. and the calculations from Ebbinghaus, decreased the accuracy of the measurements. Gindorf et al. [75] used conditions of particular interest for fuel cell applications (water vapor of 0.02 bar and oxygen partial pressures of 0.21 bar) and Ebbinghaus extrapolated data from a narrow range of temperatures between 408 and 458 K based on results from Glemser and Mueller [82] for the reaction CrO$_3$(g) + H$_2$O(g) $\rightleftharpoons$ CrO$_2$(OH)$_2$(g).

The volatility of CrO$_2$(OH)$_2$(g), apart from toxic emissions from MSW, is also important for high temperature corrosion on stainless steel. Using thermodynamic data on CrO$_2$(OH)$_2$(g) to calculate the decrease in thickness of the chromium oxide layer of stainless steel in a recovery boiler shows that the loss is about 0.1 µm per 24 h under optimal equilibrium conditions (see Figure 9). Although the real loss of the chromium oxide layer probably is significantly lower, still, chemical equilibrium model calculations can increase the knowledge of high temperature corrosion, provided reliable thermodynamic data is used.
Figure 9. Loss of Cr₂O₃(s) from stainless steel as saturated CrO₂(OH)₂(g) from a recovery boiler, using data on CrO₂(OH)₂(g) from Ebbinghaus.

However, conflicting data for Cr₂O₃(s) in the literature strongly influences the results of chemical equilibrium calculations for CrO₂(OH)₂(g). The differences between databases and data found in the literature are shown in Figure 10. The largest difference in absolute G-values was found to be about 12 kJ/mole.

Figure 10. Difference in absolute G-values with temperature for Cr₂O₃(s), using data from the HSC [69], SGTE [68], FACT [67] and IVTANTHERMO [73] databases, data from Ebbinghaus (i.e. data from the tables of JANAF [79]) and data from the tables of “Thermochemical data of pure substances” by Barin [78]. The differences are calculated using G-values from Barin as a reference. Standard deviations were calculated using S and H-values from JANAF.
4 Fate of Cu, Cr and As and other trace elements

The fate of Cu, Cr and As was determined in bottom ash, in coarse and fine ash particles, and to some extent also in gaseous emissions. The fate in all different ash fractions, i.e. bottom ash, and coarse and fine particles, was studied from bench scale (15 kW) combustion experiments (paper II). The fate in bottom ash was studied in more detail in laboratory scale (single particle batch) combustion experiments (paper III) and the fate in fine particles was further studied from large scale (65 MW) combustion (paper IV).

4.1 Bench scale (paper II)

The fate of copper, chromium and arsenic during combustion of wood impregnated with chromated copper arsenate (CCA) and a mixture of impregnated wood and peat was studied in paper II. Previous work on retention of arsenic and chromium have considered the effectiveness of different mineral sorbents and compounds in removal of metals by means of physical adsorption, chemisorption, chemical reaction, or a combination of these [54, 62-65, 83-86]. This together with earlier results [87] indicates that minerals in peat potentially could retain some of the metals, or other peat constituents could react with the metals and form stable refractory solid phases.

Co-combustion with two different peat fuels was performed where the produced ash samples were studied both experimentally with SEM/EDS and XRD analysis and theoretically with chemical equilibrium calculations. The latter were performed in two steps to be able to simulate the results for both the combustion zone (bottom ash and volatile species) and the flue gas zone (fine particles and volatile species). The fuels were pelletized and combusted in a commercial residential pellet furnace (15 kW) with under-feeding of the fuel to represent a grate fired unit used in full scale applications. During the experiments, continuous gas measurements of O₂, CO, SO₂ and NO were performed by electrochemical sensors, and samples from the flue gas were collected using a cyclone with a cut off of 7 µm placed before a total particulate matter filter. The particle mass size distributions were determined by isokinetic sampling using a 13-steps low pressure cascade impactor. The bottom ash and the impactor-samples were analyzed for crystalline phases using XRD. The bottom ash, the particulate matter filter ash and the impactor samples were also analyzed for total elemental composition using ICP-AES for the first two ashes and SEM/EDS for the third.

Results from equilibrium calculations were compared with the experimental data. Figure 11 shows the results from chemical equilibrium calculations and experimental data for the bottom ash. The comparison showed that the behavior of ash forming elements could for most parts be described by chemical equilibrium calculations.
Figure 11. Distribution of copper (top), chromium (middle) and arsenic (bottom) in bottom ash from chemical equilibrium model calculations for combustion of pure CCA-wood, 50% CCA wood mixed with peat from Norrheden, and CCA wood mixed with peat from Omberg. Red circled phases are in agreement with XRD results.

The experimental result for the fly ash particles showed that part of the volatilized chromium was identified in the fine particles as Cr(VI), presumably as alkali chromates. The volatilized arsenic was identified as As₂O₃(s) and KH₂AsO₄(s), where the latter (as K₃AsO₄(s)) was predicted by chemical equilibrium calculations (see Figure 12).
The volatilization and retention in bottom ash of Cu, Cr and As was also calculated both experimentally and with chemical equilibrium model calculations (see Figure 13). The chemical equilibrium model calculations showed that the volatilization is clearly affected by temperature, especially for arsenic and chromium. The experimental results showed that the retention of copper, chromium and arsenic was about 50-70, 100, and 30-40 %, respectively. The result from the fine particles confirmed these volatile behaviors. The coarse fly ash and the vapor phase are not included, which explains some of the discrepancies in mass balance. However, the discrepancies probably depend mainly on the variation of concentrations in fuels.

Co-combustion CCA-wood with peat generally resulted in some stabilization of the refractory phases formed during combustion of pure CCA-wood and thus a small but noteworthy decrease in volatilization of all three elements was observed.
Figure 13. (a) Chemical equilibrium model volatilization of copper, chromium and arsenic. The ranges illustrate the effect of temperature from 950-1250°C, with higher volatilization at higher temperatures. (b) Experimentally observed retention of copper, chromium and arsenic in the bottom ash. For chromium, all fuels except CCA+Omberg 20/80 exceed 100 % retention. (c) Experimentally obtained volatilization of copper, chromium and arsenic. Dark grey = CCA; Light grey = CCA+Norrheden peat 50/50; Stripes = CCA+Norrheden peat 20/80; Small dots = CCA+Omberg peat 50/50; Squares = CCA+Omberg peat 20/80
4.2 Laboratory scale (paper III)

Since a burning fuel particle undergoes several, more or less separate stages during combustion, local chemical equilibrium calculations were performed to model these sequential process conditions in paper III. The results were compared to both global chemical equilibrium calculations and experimental results.

The stages during combustion together with chemical equilibrium calculations steps are illustrated in Figure 14. During the first combustion stage, the fuel particle is heated and dried. The temperature of the fuel particle thereafter rapidly increases, leading to the devolatilization stage, which progresses under only limited access to oxygen. The next stage is the char burning stage, followed by the post-combustion stage with final ash volatilization and mineralization.

The main difference between global and local chemical equilibrium calculations is the volatilization of arsenic, 0.46% versus 68% respectively, at 1000°C. In the local chemical equilibrium calculations more than 99% of arsenic was volatilized during the devolatilization stage, when the access of oxygen is limited, and thus the formation of refractory metal arsenates is restrained. Since arsenic plays a major role in the formation of refractory phases, this difference leads to formation of stable calcium, magnesium and alkali arsenates in the local chemical equilibrium calculations, with no arsenic left to form the less stable chromium and copper arsenates. These latter phases are however formed in global chemical equilibrium calculations. As a consequence, the formed copper and chromium phases differ significantly between global and local chemical equilibrium calculations (see Figure 15).
Moreover, a comparison between chemical equilibrium calculations and experimental results indicated that the combustion of CCA-wood particles is a result of three partially overlapping stages: devolatilization, char burning and post-combustion. Thus, the reality could be described as a mix between global and local chemical equilibrium calculations. For example, at lower temperatures, arsenic volatilization can be more accurately modeled by global equilibrium calculations, while at higher temperatures local equilibrium calculations are more adequate (see Figure 16). Other examples are Cu₃(AsO₄)₂(s) that was only predicted in global chemical equilibrium calculations whereas both MgCr₂O₄(s) and CuCr₂O₄(s) were only predicted in local chemical equilibrium calculations. However, all these three phases were found in XRD analyses (see Figure 15).

**Figure 15.** Distribution of copper (top), chromium (middle) and arsenic (bottom) during global chemical equilibrium calculations and local chemical equilibrium calculations i.e. the char burning stage and the post-combustion stage. Red circled phases are in agreement with XRD results.
Figure 16. Volatilization of arsenic (left) and chromium (right) species during combustion of impregnated wood. Predictions from local chemical equilibrium calculations (light grey), global chemical equilibrium calculations (black) and experimentally measured (grey striped).

4.3 Full scale (paper IV)
The fate of harmful trace elements and sodium and potassium in fine particles during full scale combustion of municipal solid waste (MSW) was studied in paper IV. Previous studies have shown that trace elements are enriched in submicron particles [30-33]. The collection efficiency for submicron particles by electrostatic precipitators is however less than for coarse particles (>1 µm). Thus, harmful elements emitted to the atmosphere from full scale combustion are probably either volatile or enriched in submicron particles.

The influence of chlorine and sulfur content in the fuel were studied using additives. Polyvinylchloride (PVC) was used as a chlorine source and waste car tires as a sulfur source. However, only limited variation was accomplished by the fuel additives.

The analyses of the size separated ash particles showed no major difference between particle size or fuel additive. Some smaller differences could however be outlined. The elemental analysis showed a slight increase in chlorine for smaller particles, especially for fuels with PVC added, and an increase in sulfur for fuel with waste car tires added (see Figure 17). The bimodal mass size distribution showed an increased amount of submicron particles when PVC was added to the fuel and a slight increase of the 2 µm particles when waste car tires were added.

The elemental analysis using ICP-SFMS showed that at least Na, K, As, Cd, Cr, Cu, Pb and Zn were found in the submicron particles. The result also shows that the content of submicron particles is dominated by Na, K and Zn with lower amount of the harmful elements Pb, As and Cu. The partitioning of elements showed that 8 % of As, 98 % of Cu, 43 % of Cr, 1.3 % of Cd, 22 % of Pb, and 20.2 % of Zn are retained in the bottom ash. Thus, Cu can not be considered a volatile element but is still found in significant amount in the fine particles. This indicates that the concentration of harmful trace elements in submicron particles is dependent on both volatility of the trace element and the trace element concentration in the fuel.
The XRD analysis identified NaCl(s), K$_2$ZnCl$_4$(s) and K$_3$Na(SO$_4$)$_2$ in all samples, with a typical distribution of 40, 30 and 30%, respectively. Other crystalline phases of trace elements were below the detection limit.

In the chemical equilibrium model calculations both NaCl(s) and K$_3$Na(SO$_4$)$_2$(s) were predicted. The latter was stable between 200 and 500°C, which also is in agreement with experimental findings since the particles were sampled above 200°C. However, thermodynamic data on K$_2$ZnCl$_4$(s) is lacking and is thus critically needed. Both zinc and potassium are predicted as sulfates, although K$_2$ZnCl$_4$(s) would be kinetically favored before the slower sulfation, since both potassium and zinc are predicted to volatilize as chlorides. However, in terms of volatility, the model results explained the experimental findings well. The results from the chemical equilibrium model calculations are showed in Figure 18.

Figure 17. Elemental analysis of ash particles using SEM-EDS.
Figure 18. Predicted distribution of Na, K, Pb, Zn, Cu, As, Cr and Cd in fine ash particles from chemical equilibrium model calculations.
5 Discussion

Although the process chemistry of copper, chromium and arsenic initially may appear very complex, some evident stability trends and patterns for the most important refractory phases could be elucidated by analyzing the full chemical equilibrium relations in detail. The analysis showed that the pure oxides of copper, chromium and arsenic are the least stable phases and thus show the highest volatility. For chromium and arsenic, which are of most concern regarding negative environmental and health effects, the interactions with copper, calcium and alkali metals were most important. The stability trends of the refractory phases are shown in Figure 19.

Increasing stability, decreasing volatilization of Cu, Cr and As

\[ \text{As}_2\text{O}_3 < \text{CrAsO}_4 < \text{Cu}_3\text{(AsO}_4\text{)}_2 < \text{Ca}_3\text{(AsO}_4\text{)}_2 < \text{K}_3\text{AsO}_4 \]

\[ \text{Cr}_2\text{O}_3 << \text{CaCrO}_3 < \text{Na}_2\text{CrO}_4 < \text{K}_2\text{CrO}_4 \]

Increasing stability, decreasing volatilization of Cu, Cr and As

Figure 19. Illustration of stability trends for Cu, Cr and As phases in a typical combustion atmosphere.

These trends clearly illustrates the results from the chemical equilibrium calculations in paper II, III and IV. Chromium and arsenic interacted with copper to form CuCrO$_2$(s) and Cu$_3$(AsO$_4$)$_2$(s). Both of these refractory phases are more stable than the pure chromium and arsenic oxides and thus suppressed the formation of volatile phases. This explains the increased formation of volatile chromium upon co-combustion of CCA-wood with the aluminum-rich Norrheden peat. When aluminum was added to the fuel, copper formed the more stable CuAl$_2$O$_4$(s) instead of CuCrO$_2$(s). Further, calcium and alkali arsenates are more stable than both CaCrO$_3$(s) and alkali chromates. Thus, chromium is left to form the least stable phase, Cr$_2$O$_3$(s).

Calcium forms refractory phases with both chromium and arsenic. Calcium arsenates are however more stable than CaCrO$_3$(s), and thereby the chemical equilibrium model calculations only predicted chromium to react with calcium for co-combustion of CCA-wood with the calcium-rich Omberg peat. It should be pointed out that the chemical equilibrium calculations overpredict the stability of calcium arsenates, which leads a discrepancy between predicted and experimental volatilization of arsenic.
Therefore, the local chemical equilibrium calculations in paper III is in better agreement with experimental findings, at least at higher temperatures.

Alkali arsenates and chromates are the most stable phases according to Figure 19. However, if sulfur and chlorine are available as in paper IV, alkali sulfates and chlorides will form since they are more stable than both alkali arsenates and chromates. This also explains the absence or only small formation of alkali arsenates and chromates in paper II and III. It should be noted that alkali chromates and arsenates are the least refractory of the phases considered and thus not suitable as additives. Also, alkali chromates retain chromium in the carcinogenic hexavalent form. Aphthitalite (K$_3$Na(SO$_4$)$_2$) identified in the submicron particle ashes could also form solid solution with K$_3$Na(CrO$_4$)$_2$ and thus constitute a possible host phase for minor amounts of hexavalent chromium [88].
6 Conclusions

Based on the separate papers included in the thesis, the following general conclusions on the fate of Cu, Cr and As, as determined experimentally and predicted by chemical equilibrium model calculations, can be outlined:

- The initial review of thermochemical databases in paper I showed that there are differences between the three databases HSC, SGTE and FACT, both in numbers of compounds and in thermodynamic data. The differences in absolute G-values were significant for most compounds although the differences were larger for gaseous species than condensed phases. The differences in thermodynamic data between databases also lead to significant discrepancies in equilibrium calculations.

- An extensive elucidation of stability aspects of different CCA phases was given in paper II. Also, the experimental results showed a small but significant decrease in volatilization of copper, chromium and arsenic when impregnated wood were co-combusted with peat. Refractory phases such as calcium arsenates and copper chromium oxides were generally identified in the bottom ash for all fuels, and only minor phase changes were observed. Identified phases for all fuels were CuCrO$_2$(s), (Fe,Mg,Cu)(Cr,Fe,Al)O$_4$(s), Cr$_2$O$_3$(s), and Ca$_3$(AsO$_4$)$_2$(s). Arsenic was also identified in the fine particles as KH$_2$AsO$_4$(s) and As$_2$O$_3$(s).

- Identified phases in the bottom ash in paper III were CuCrO$_2$(s), CuCr$_2$O$_4$(s), MgCr$_2$O$_4$(s), Cr$_2$O$_3$(s), Ca$_3$(AsO$_4$)$_2$(s). The chemical equilibrium model calculations also predicted these phases. However, some phases were predicted in the global chemical equilibrium model calculations and some other phases in the local chemical equilibrium model calculations. This indicates that the reality can be described as a mix between global and local chemical equilibrium calculations.

- The semi-quantitative XRD analysis identified three phases in the submicron particles collected from the raw flue gases during full scale combustion of MSW in paper IV. These were NaCl(s), K$_2$Na(SO$_4$)$_2$(s) and K$_2$ZnCl$_4$(s). Other harmful trace elements identified from ICP-SFMS analysis of the fine particles were As, Cd, Cr, Cu, and Pb. No phases of these elements were identified in XRD since the amounts were below the detection limit. Chemical equilibrium model calculations predicted all elements to be volatile, which agrees well with experimental findings. Both NaCl(s) and K$_2$Na(SO$_4$)$_2$(s) were predicted as stable phases at low temperatures. However, thermodynamical data on K$_2$ZnCl$_4$(s) is critically needed.

- The comparison between experimental and predicted results showed that the predicted results generally agreed well with experimental results.
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Fate of Cu, Cr, As and some other trace elements during combustion of recovered waste fuels

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