FRACTIONATED HEAVY METAL SEPARATION AND ASH UTILIZATION IN BIOMASS COMBUSTION AND GASIFICATION PLANTS

I. Obernberger, J. Dahl

TECHNICAL UNIVERSITY GRAZ,
DEPARTMENT OF CHEMICAL ENGINEERING

Contract JOR3-CT95- 0001

FINAL PUBLISHABLE REPORT

January 1, 1996 to June 30, 1998

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non-Nuclear Energy Program
JOULE III

Table of contents

Fractionated Heavy Metal Separation and Ash Utilization in Biomass Combustion and Gasification Plants

Abstract

Previous research has shown that an entire recycling of biomass ash cannot be recommended due to environmental pollution by heavy metal depositions in the forest ecosystem via air and rain. Consequently, it is necessary to separate a small side stream as rich in heavy metals as possible in order to be able to utilise the largest amount of biomass ash produced. The more effectively this heavy metal fractionation works in practice, the higher is the concentration of heavy metals in the small ash fraction that has to be separated.

Consequently, comprehensive full-scale and bench-scale test runs were performed in three straw incinerators, one wood-fired CFB combustion unit, one wood-fired fixed-bed gasification unit, one bark-fired CFB gasification plant, and a bench-scale BFB combustion reactor in order to investigate the possibilities and the potential of the technique of fractionated heavy metal separation. Prior to the test runs, standard methods for sample taking, sample preparation and analyses of ash-forming and trace elements in biomass fuels and ashes were established by the performance and the evaluation of an international Round Robin on biomass fuel and ash analyses. This Round Robin provided the basis for correct and representative analytical results and allowed for reliable comparison of the data obtained by the project partners.

The experimental results achieved were accompanied by aerosol measurements, investigations concerning aerosol formation as well as by chemical equilibrium mode calculations for heavy metals and ash-forming elements in biomass combustion and gasification plants.

The results from elemental mass balances revealed that the environmentally most relevant heavy metal, Cd, is depleted in the bottom ash in all processes investigated and is mainly found in fly ashes precipitated downstream the boiler section. This fact indicates that Cd is vaporised at high temperatures and under reducing conditions as present in and around burning fuel particles and then undergoes condensation on, or reactions with, the surface of fly ash particles. Aerosol measurements and modelling indicated that the vaporised heavy metals mainly undergo surface reactions with coarse fly ash particles at high temperature prior to condensation. This makes high temperature separation of heavy metals from fly ash particles in the combustion plant itself difficult at temperatures below 850°C. Most biomass-fired CFBC units operate at or below 850°C and, therefore, a useful fractionation within CFBC seems difficult. In grate-fired biomass combustion units the combustion temperature is higher and the bottom ash is not diluted with bed material (like in CFB plants), which creates a very high potential for fractionated heavy metal separation. Based on these results, several possibilities of utilising and enhancing the fractionation in biomass-fired grate combustion units were derived.

Moreover, basic laboratory research on the possibilities and the potential of heavy metal recovery from highly contaminated fly ash fractions by thermal ash treatment and biochemical leaching have revealed promising results and offer possibilities for heavy metal recovery from contaminated biomass fly ashes, thus completely avoiding ash disposal.

Partnership

Co-ordinator	Abbreviation	Contact person
Institute of Chemical Engineering, Technical University Graz, Inffeldgasse 25, A-8010, Graz, Austria	TUG	Dr. Ingwald Obernberger

Project partners	Abbreviation	Contact person
Vattenfall Utveckling AB Jämtlandsgatan 99 P.O. BOX 513 S-16215 Vällingby, SWEDEN	VAT	Dr. George Sfiris
Danish Boiler Owner's Association, dk-TEKNIK Energy and Environment 15 Gladsaxe Møllevej DK-2860, Søborg, DENMARK	DKT	Anders Evald
Technical Research Center of Finland (VTT), Chemical Technology P.O.Box 1401, FIN-02044 VTT, ESPOO, FINLAND	VTT	Terttaliisa Lind
Department of Inorganic Chemistry University of Umeå, Energy Technology Centre, Box 726 S-941 28 Piteå, SWEDEN	UME	Prof. Anders Nordin

Technical Description

Introduction and objectives

As the energy utilisation from biomass in district heating or co-generation (combined heat and power production) plants represents one important possibility to reduce the CO_2 emissions, the importance of this technique for energy production is of growing importance on a European level. The increasing use of biomass fuels in combustion / gasification units will also lead to an increase in the amounts of ashes produced. The development of adequate techniques to reduce the amounts of non-recyclable ashes allows, on the one hand, to save disposal area as well as disposal costs and, on the other hand, to improve the general public's acceptance of energy utilisation from biomass. The knowledge about technological possibilities / requirements and the potential of fractionated heavy metal separation for different combustion / gasification technologies and the use of different biomass fuels were the main objectives of the project.

In detail, special attention was given to the following points:

1) Co-ordination and standardisation of methods for ash and fuel sampling, sample preparation (homogenisation) and the complete detection of elements in ashes and biofuels in order to guarantee correct and representative results and allow for reliable comparison of the analytical data obtained by the project partners.
2) Comprehensive test runs to investigate the possibilities and the potential of the technique of fractionated heavy metal separation in two straw-fired grate incinerators, one wood-fired CFB combustion unit, one wood-fired fixed-bed gasification and one bark-fired CFB gasification plant. Furthermore, results for moving-grate furnaces fired with wood chips and bark available from an Austrian research project were implemented in order to make this technology applicable to all EU countries.
3) Basic research on modelling high-temperature equilibria and on the condensation / aerosol formation of easily volatile heavy metals and ash-forming elements in flue gases of combustion / gasification plants in order to be able to explain the experimental results and to derive generally or specifically valid functional correlations. This research on modelling was supported by large-scale and pilot-scale experiments for parameter adaptation.
4) Basic laboratory research on the possibilities and the potential of heavy metal recovery from highly contaminated fly ash fractions by thermal and biochemical ash treatment in order to recycle raw materials and to completely avoid ash disposal.

Moreover, the dissemination of results concerning possibilities of sustainable biomass ash utilisation among plant manufacturers, utilities, authorities and farmers as well as the support of technological applications was a key issue.

The methods proposed for heavy metal recovery from highly contaminated filter fly ashes can also be seen as a contribution to close the elementary cycles of nature within the course of thermal biomass utilisation and to form the basis for appropriate technologies.

The evaluation of the data gained from large-scale, pilot-scale and laboratory-scale test runs were used to improve existing computer models simulating aerosol formation and heavy metal behaviour. The results achieved make it possible to predict the composition of the different ash fractions and the material fluxes of environmentally relevant heavy metals within biomass combustion / gasification processes. Thus, these measurements and calculations are of great interest for the design and planning of future biomass combustion / gasification systems as well as for the choice of biomass fuels and thermal conversion technologies posing the least technological and ecological problems.

Co-ordination and standardisation of sampling and analysis of biomass ash and fuel samples co-ordinated by TUG

The standardisation of sampling, sample preparation and analytical techniques was performed and completed in the first year of the project. The results and evaluations of this work are reported in a separate report named "Biomass fuel and ash analysis" and published by the European Commission [1]. The main work carried out and the results achieved can be summarised as follows:

As part of this project, and in co-operation with the IEA Bioenergy Agreement, TASK XIII, Activity 6 “Integrated Bioenergy Systems“, 16 laboratories participated in the Round Robin on biomass fuel and ash analysis.

The objective of the Round Robin was to provide a basis for establishing international standards for the correct and complete detection of trace elements in biomass fuels and for the reliable detection of elements in the different ash fractions produced in biomass combustion/gasification plants, covering all the important analytical steps, sample homogenisation, sample digestion and analysis itself.

Four fuel samples (milled and unmilled samples of straw and bark), four ash samples (bark bottom ash, bark and straw fly ash, condensation sludge) and two digest solutions (from the milled straw and from the condensation sludge) were investigated in the Round Robin. The fuel samples were analysed for their concentrations of water, Ca, P, K, S, Cl, Zn, Pb, Cd, Cu, and the total ash content. The ashes were analysed for their concentrations of water, Ca, P, K, S, Cl, Zn, Pb, Cd, Cu, $C_{combustible}$ and C_{CO2}, and the digest solutions for the parameters Ca, P, K, S, Zn, Pb, Cd, and Cu. All participating laboratories were free to choose the respective analytical methods, only recommendations and information concerning available experience and possible problems that might occur in certain cases were supplied.

The results from the participating laboratories were statistically evaluated for intra- and interlaboratory outlier values with a distribution-free method called Huber’s method. The reason for using the Huber's outlier test and not the common ISO 5725 method was that in this Round Robin the participating laboratories were using the procedures and methods they have experience with and that they normally use for biomass fuel and ash analyses. Consequently, the results were not obtained using the same protocol for a certain analysis and therefore a robust method based on the median value instead of the average (mean) value was required for the statistical evaluation. The results of all participating laboratories were treated equally in this evaluation, the resulting medians were used as guiding values for the probably true values. Moreover, homogeneity tests for several biomass samples used in the Round Robin were performed separately. Subsequently, an analytical evaluation was performed by comparing the different methods and the equipment used for sample homogenisation, digestion and analyses with the results achieved. The results of the statistical as well as the analytical evaluation are shown in diagrams and tables for all samples and all elements investigated. In addition the most important outcomes are discussed separately for biomass fuels and ashes, distinguishing in both cases between the homogenisation, the digestion and the analysis step and between specific problems that occurred for certain elements.

Finally, in order to complete the evaluations, to discuss the results with the participating laboratories and to ensure that the accuracy and comparability of analytical results will fulfil the technological requirements for the calculation of material balances for ash-forming elements in biomass combustion/gasification plants, an analysis meeting was held where the outcomes of the Round Robin were discussed for the biomass fuel as well as for the ash samples element by element.

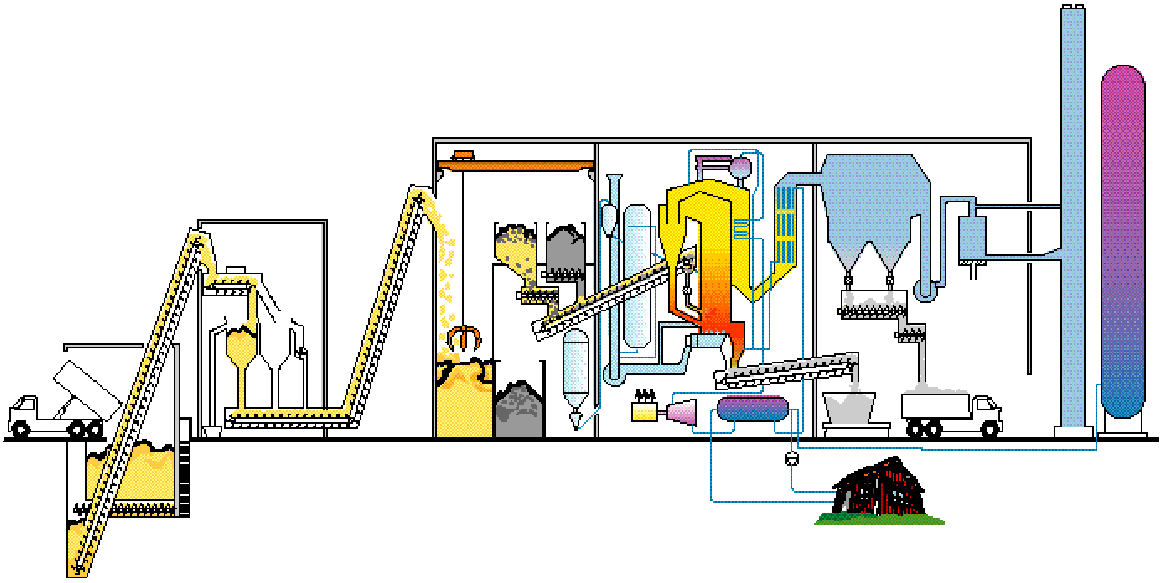
Full-scale test runs in circulating fluidised bed (CFB) combustion and gasification by partner VAT

Material fluxes and the behaviour of heavy metals (Cd, Pb, Cu and Zn) during combustion and gasification of biomass fuels was studied during three experimental periods. Combustion of forest residues and willow (*Salix*), respectively, was studied at a 30 MW CFB boiler at the Nässjö kraftvärmeverk, Nässjö, Sweden. Gasification of bark was studied at a 35 MW CFB gasifier at the Värö bruk, Väröbacka, Sweden. The main objective of the experiments was to study the material flows during combustion and gasification, respectively, and to establish energy balances. The composition of different material fractions (fuel, ash and bed material) was investigated, with a special focus being placed on heavy metals. Operating data, such as heat and power output, primary and total airflow, temperature profiles as well as pressure and flue gas composition, were recorded continuously.

In the following a short description of the FB units where the full-scale test runs took place is given.

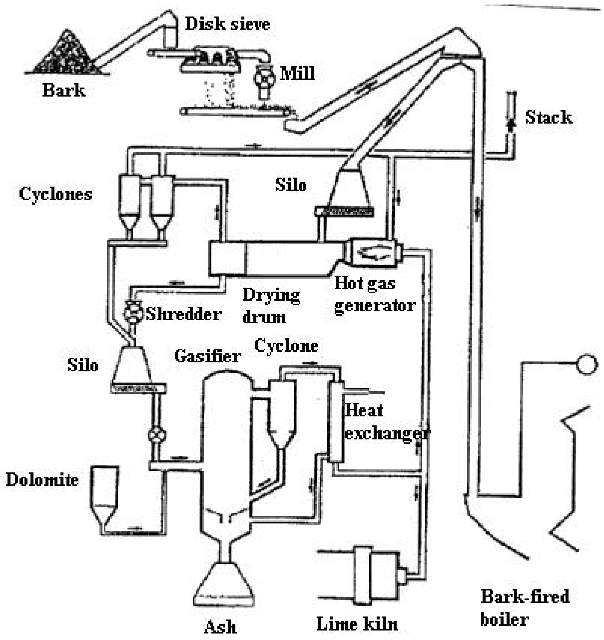
The Nässjö Kraftvärmeverk was commissioned in 1990. The plant comprises sections for fuel delivery and preparation, a CFB boiler, flue gas purification and condensing equipment, plus a section for power generation with a steam turbine and a district heat condenser (Figure 1). The production capacity of the solid fuel boiler is 20 MW of heat and 9 MW of electricity. The CFB boiler is designed for the combustion of peat, wood chips and coal. The flue gas condensing equipment yields some 6 MW of heat at full load. The electrostatic precipitator separates about 99% of the fly ash. The fly ash is collected in an ash silo. A scraper conveyor transports the bottom ash from the bed discharge opening to a hopper.

Figure 1: Schematic view of the Nässjö Kraftvärmeverk



The Värö Bruk is a pulp mill in the west of Sweden. The plant includes a gasifier, which has been in operation since 1987. The gasification system comprises fuel delivery, fuel preparation, fuel drying, a 35 MW CFB reactor and equipment for ash removal. (Figure 2). The reactor is designed for the gasification of bark, forest residues or sawdust. The gasifier converts bark into low-value gas, which is used as a fuel for the lime kiln and the fuel drier. The bark is dried in a rotating cylindrical drum, the final moisture content being typically 10 to 15%. The ash removal system collects bottom ash from the reactor and transports it to a hopper, where water is added to the ash.

Figure 2: The gasification unit at the Värö bruk.



Full-scale test runs in fixed-bed biomass combustion and gasification plants by partner DKT

A total of four full-scale test periods in three different straw-fired fixed-bed combustion systems were performed. Except the two full-scale experiments performed as part of the JOULE III project, one additional experiment financed by SK-Power, a Danish utility company, and one additional experiment financed by the Danish Energy Agency were carried out. The experiments were aimed at providing general figures about the trace element fractionation in the different ash fractions, at achieving further understanding on the processes influencing fractionation (especially in the combustion zone), and at obtaining general figures on the mass of each ash fraction produced.

Table 1: Plant data on Danish full-scale test runs in straw-fired grate combustion plants

Explanations: CHP...combined heat and power

Plant and test period	Technology	Plant size [MW]	Fuel
Masnedø	CHP grate-fired	20.8 (heat) 8.3 (el.)	Straw
Høng 1	grate-fired	6.3	Straw
Nr. Aslev	cigar-fired	2.5	Straw

In the experiments all flows of fuel and ashes were determined by weighing over an 8-hour period and samples were taken to determine trace element concentrations in the fuel and ash fractions. Operating data, such as heat and power output, temperature profiles as well as pressure and flue gas composition, were recorded continuously during the test runs.

A similar full-scale experiment on a 100 kW wood chip-fired two-stage fixed-bed gasifier system was performed at the Danish University of Technology, Lyngby, Denmark, and comprised more than 3 days of measurements.

Chemical equilibrium model calculations and bench-scale isothermal reactor experiments by partner UME

Previous experimental results from full-scale combustion trials [2] have indicated that a significant separation of heavy metals from the bulk ash may be obtained at high temperature because of the lower volatilisation temperature of these metals, compared to the major ash-forming elements, Ca, Si, P and Mg.

The objective of UME was therefore to further evaluate the potential of this idea by means of both theoretical state-of-the-art chemical equilibrium model calculations and corresponding controlled experiments in a bench-scale isothermal fluidised-bed reactor.

For evaluating the theoretical potential of fractionated heavy metal separation, as well as for designing appropriate experimental set-ups for further feasibility studies, chemical equilibrium model calculations may initially be used. In contrast to coal, where most ash-forming elements are mineral bound, biomass has the advantage that most of the ash-forming elements are organic matter or ion bound in the fuel [3, 4]. This implies that the reactivities and reaction rates for all elements can be expected to be relatively high, making an initial equilibrium approach highly justified.

The chemical equilibrium calculations were performed using the program ChemSage 4.1, and the database of the Scientific Group Thermodata Europe (SGTE), which was expanded by additional data in order to be able to include as many relevant species as possible. Because of the very limited data on heavy metal solubility in the many potential ash systems presently available, it was decided not to consider any solutions in the present work.

Sensitivity analyses of chemical equilibrium calculations and parameters influencing heavy metal fractionation

Previous work indicated the possibility of using a high-temperature cyclone for separation of condensed nutrients while the heavy metals still are in the gas phase. However the volatilisation temperature for the different heavy metals varies significantly with both the fuel variables and operating conditions. A systematic sensitivity analysis was therefore performed to determine the effects of these variables and inaccuracies in thermochemical data on the theoretical volatilisation temperatures of five metals (Cd, Pb, As, Zn and Cr) by utilising underlying fractional factorial designs to structure the chemical equilibrium calculations [5, 6].

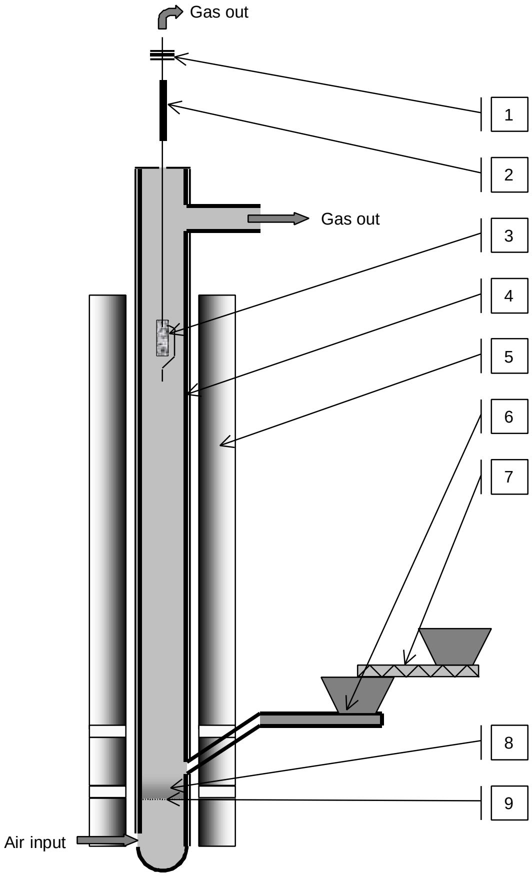
The levels of thermochemical data were taken from reported inaccuracies in $\Delta fH°(298)$ and $S°(298)$, so that the maximum inaccuracies in Gibbs free energy ($\Delta fG°$) for every heavy metal species were obtained. Carbon-to-oxygen ratio (COR), hydrogen-to-oxygen ratio (HOR), fuel moisture (H_2O), Cl, S, As, Cd, Cu, Pb and Zn levels were selected to cover a wide range of biomass fuels and taken from the expanded biomass database presented by Nordin. Extreme values in the fuel characteristics were excluded. The air-to-fuel ratio (AFR) was varied from 1.05 to 2 times that theoretically required for stoichiometric combustion.

Bench-scale experiments in an isothermal reactor

Although full-scale experiments are valuable for problem identification and of course crucial as final confirmation tests, they often involve too high experimental costs, memory effects, uncontrolled, varying and unknown local conditions to be applicable to mechanistic or

initial/feasibility studies. Consequently, in parallel to the large-scale fluidised-bed combustion test runs performed by VAT, corresponding bench-scale bubbling fluidised-bed (BFB) experiments were performed by UME, using the same fuels. The objectives of the bench-scale experiment were therefore (i) to determine the separation efficiency under controlled bench-scale and isothermal conditions and (ii) to try to determine the influence of temperature and air-to-fuel ratio on the degree of heavy metal volatilisation/re-condensation. In addition, the chemical equilibrium effects, considering also some of the most important complex compounds between heavy metals and major ash-forming elements, could be illustrated.
An isothermal fluidised-bed reactor was constructed (see Figure 3).

Figure 3: Outline of the isothermal reactor used for bench-scale combustion experiments



Explanations:
(1) filter
(2) dilution section
(3) cyclone
(4) ceramic lining
(5) wall heater
(6) vibration feeder
(7) screw feeder
(8) bed
(9) distribution plate

The reactor tube of alumina-lined steel is 88 mm in diameter and 2,300 mm long. A distribution plate of alumina with 1.5-mm holes and a total of 2.6 percent open area is used to fluidise a bed of quartz sand. The whole reactor tube, including a reversed cyclone-like air pre-heater, the bed section and the distribution plate is externally heated and temperature controlled.
The biomass fuels investigated were collected during the full-scale test runs conducted by VAT at Nässjö CFB combustion plant, during April 1996 (forest residues) and March 1997 (willow, *Salix*). Fuel samples were taken continuously, during the full-scale test days. The materials were then homogenised and sent for analysis.
Effects of process temperature and air-to-fuel ratio were determined by varying the investigated temperature levels to 800, 850 and 900°C and the air-to-fuel ratio levels to 0.6, 0.9 and 1.7 for test runs with *Salix*. The test series with forest residues were only varied in temperature, but in a wider interval (750, 850, 950°C). Only primary air and a constant air-to-fuel ratio corresponding to measured exit oxygen concentrations of 8 Vol% (wet flue gas) were used. In order to try to differentiate and sample representative hot cyclone fly ashes and

filter ashes after controlled condensation of the metals, a special sampling probe consisting of a pre-cyclone, a dilution probe and a quartz filter was used.

All fuel and ash samples were analysed using the laboratories, sample preparation procedures and analytical methods as suggested by the previously described Round Robin.

Comparison between experiments and chemical equilibrium model calculation results

A comparison between results from chemical equilibrium model calculations and experimental results from laboratory-, bench- and different full-scale test runs was performed. The predicted general fates of As, Cd, Cu, Pb, and Zn were calculated and compared specifically with the different experimentally determined separation efficiencies. The extremely reducing conditions in the pyrolysis of the fuel particles and the generally reducing conditions in the section below the secondary air inlet were initially studied, followed by material fractionation into the different plant-specific stages, depending on air and temperature distributions. In the present work UME found a general screening of temperature and total air-to-fuel ratio (λ) to be sufficient. Temperature and λ were generally varied from 500 to 1,200°C and 0 to 2.0 respectively, where zero lambda is assumed to represent the conditions close to those within the burning hot fuel particles.

Measurements and model calculations of particle and aerosol formation during biomass combustion by partner VTT

During solid fuel conversion, i.e. combustion and gasification, the ash-forming compounds are transformed in many ways. Ash-forming compounds include matrix elements and trace elements. Heavy metals are usually present in the fuel in small quantities, which makes them typical trace elements. The transformation mechanisms determine the fractionation of the ash-forming compounds into the bottom ash, different fly ash fractions, and inorganic vapours. In addition, the toxicity of a heavy metal is dependent on its speciation in the ash, and consequently, the specific path leading to the formation of that species. Therefore, mechanistic understanding of the heavy metal transformations during combustion and gasification is needed in order to develop a sustainable conversion cycle with environmentally acceptable heavy metal levels in the ash.

In this work, VTT studied the behaviour of Cd, Cu, Pb and Zn during circulating fluidised-bed combustion and gasification of wood-based biomass fuels both experimentally and with aerosol modelling. Special emphasis was placed on the volatilisation behaviour and subsequent transformations of the heavy metals. For describing the transformations of the volatilised species, a conceptual aerosol model was developed. The aerosol model, combined with experimental results, was used to determine the gas-to-particle conversion mechanisms of the volatilised species.

The experimental part of the investigation was carried out at two full-scale biomass conversion plants. Heavy metal behaviour during circulating fluidised-bed combustion (CFBC) of forest residues and willow was measured at a combined heat and power plant during VTT’s full-scale tests at Nässjö Kraftvärmevärk in Sweden. The gasification measurements were also carried out at the circulating fluidised-bed (CFB) bark gasification of Värö bruk plant during VAT’s full-scale test runs. During all the measurements the process conditions were kept stable.

A dilution probe was developed to sample aerosols, i.e. particles and vapours, from the flue gas channel at temperatures up to 900°C. In the dilution probe, the sampled gas was simultaneously diluted and cooled by introducing dilution gas into the sample through a porous tube. With the dilution gas and the cooling gas, the temperature of the sample leaving the dilution probe could be regulated. The mass size distributions of the fly ash particles were determined by collecting size-classified aerosol samples with an 11-stage, multi-jet compressible flow Berner-type low-pressure impactor [7, 8] upstream and downstream of the convective back pass at temperatures of 810-830°C and 150°C, respectively. Samples were taken with the low-pressure impactor upstream of the convective pass during combustion and at both locations during gasification; subsequently, the hot flue gas was diluted. A pre-cutter cyclone was used before the dilution probe inlet to collect particles larger than 2 µm (see Figure 4). The total mass of solid particles in the hot flue gas was measured by using hot quartz fibre filters at the same high temperatures as in the duct. The filters therefore only collected particles in the flue gas and let gaseous species pass through. Downstream of the convective pass the low-pressure impactor was inserted into the flue gas channel during the combustion test runs. For the measurements during combustion of forest residues, a pre-cutter cyclone with Stokes cut diameter of 5.4 µm was used upstream the low-pressure impactor in order to avoid overloading of the upper impactor stages (see Figure 5). During willow combustion, the particle mass loading was so low that no pre-cutter cyclone was needed.

Figure 4: **Schematic picture of the sampling set-up for the low-pressure impactor at T = 810-830 ℃.**

Explanations: The impactor collections were carried out after dilution of the aerosol.

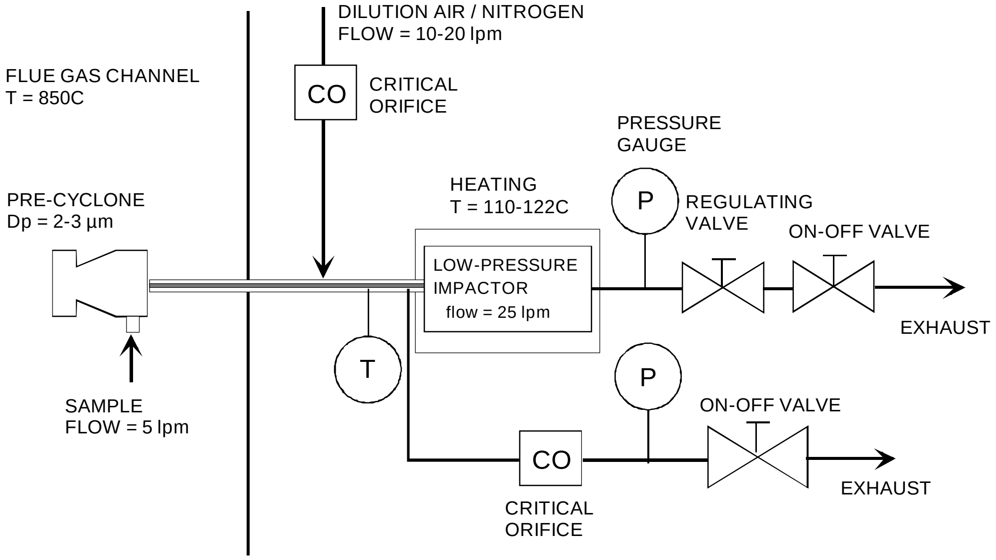
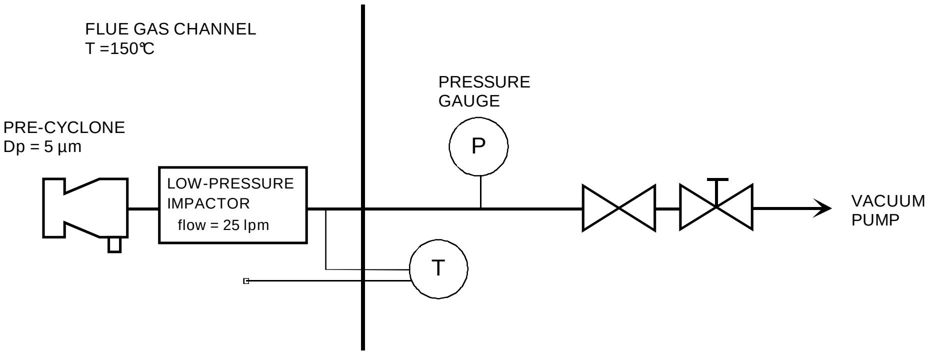


Figure 5 **Schematic picture of the sampling set-up for the low-pressure impactor at measurement location #2 downstream of the heat exchanger section during combustion.**

Explanations: The impactor was situated inside the flue gas channel. During combustion of willow, no cyclone was used. The impactor was inserted in the flue gas channel to face the flue gas flow.



The size distributions of the cyclone-collected particles were measured using the Coulter LS 130 laser diffraction method. The samples collected in the cyclone and with the impactor on polycarbonate substrates were analysed for Na, Mg, Al, Si, P, S, Cl, K, Ca, Cu and Zn with instrumental neutron activation analysis (INAA) and particle-induced X-ray emission analysis (PIXE). Cd and Pb were analysed with graphite-furnace atomic absorption spectroscopy (GFAAS). The major crystalline ash compounds in the fly ash samples were determined using X-ray diffraction (XRD). The speciation of Cd and Zn in the fly ash from CFB combustion of willow was determined with X-ray absorption fine structure spectroscopy (XAFS).

Recovery of heavy metals by thermal ash treatment by partner TUG

The project aimed at investigating parameters that influence the vaporisation of heavy metals from contaminated biomass ashes in order to reveal the potential of a thermal treatment method suitable for heavy metal recovery from contaminated biomass ashes. The investigation primarily focused on the heavy metals Zn, Cd, and Pb, but also covered the heavy metals As and Cu. The scope of work also included the design of a possible process for thermal ash treatment in order to obtain a non-toxic ash fraction that can be returned to forest soils or agricultural fields.

Therefore, the reduction goals were set according to the corresponding Austrian guidelines for biomass ash utilisation [9, 10]. The heavy metals recovered should be gained in a form suitable for utilisation in the metallurgical industry.

The experimental set-up used for laboratory experiments is outlined in Figure 6. The main components are a vertical tube oven (C in Figure 6) with an ash container designed to let the purge gas pass through the ash sample (B in Figure 6). Vaporised compounds are precipitated on the water-cooled surface (A in Figure 6) or in the gas washing bottle (D in Figure 6).

An advantage of this equipment is the good contact achieved between the purge gas and the ash sample, increasing the diffusion rate of volatilised compounds from the ash particles to the gas boundary layer.

The inner quartz tube and the ash crucible were inserted into the cold oven (25°C), which was subsequently heated up to the target temperature (780-1,000°C). The target temperature was reached after 20 minutes and then kept constant (deviation of +/- 2°C) for 1.5 h before the oven was turned off. The temperature of the cold finger in the precipitation unit was kept constant throughout the experiment by circulating water with a constant input temperature of 50°C through the "cold finger". The inlet water was maintained at a constant temperature by passing it through a thermostatically controlled tank.

Two gases were used in the experiments: pure nitrogen (N_2) and air. The gas velocity was kept at 0.002 Nm^3/h during all experiments performed.

All precipitates were completely dissolved in a sub-distilled 6% HNO_3 solution after each experiment (the same acid that was also used in the gas washing bottle).

Fly ashes from three different biomass combustion plants were selected for the investigations: a condensation sludge (CS-G) and an ESP fly ash from Austrian grate-fired biomass combustion plants (ESP-G) burning bark and wood chips, respectively. Furthermore, an ESP fly ash from a Swedish CFBC plant utilising forest residues was included, (ESP-CFB). The ashes were chosen because of their high concentrations of heavy metals, but also due to their different compositions concerning major matrix elements (see Table 2).

As a result of residuals of unburned carbon in the ash samples, a local reducing atmosphere is created while glowing the ash. The combustible carbon reduces oxides in the ash samples, among those heavy metal oxides (Equation 1 and 2). Due to the fact that metallic Zn and Cd are significantly more volatile than their respective oxides, the vaporisation of these metals is enhanced by the reactions with C_{comb}.

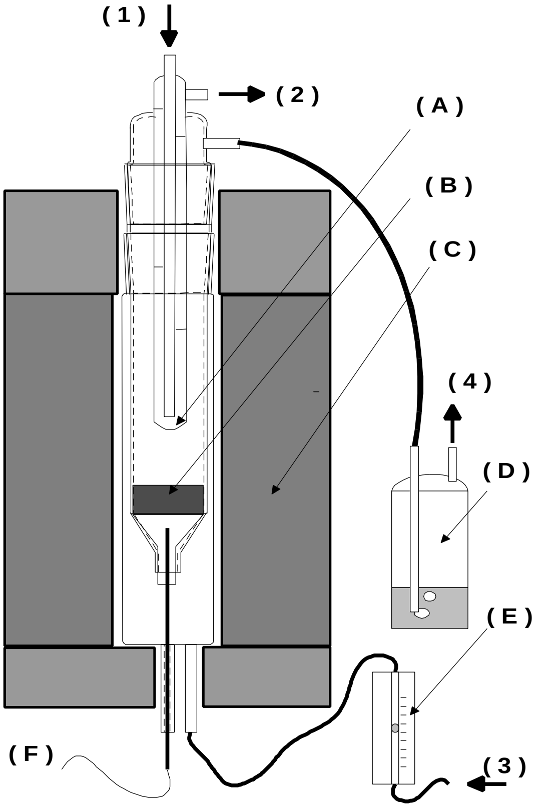
$$MO + C \Rightarrow M + CO(g) \qquad \textbf{Equation 1}$$

MO + CO(g)=>M + CO_2(g) **Equation 2**

M= Zn, Pb and Cd

The effect of an increased reducing atmosphere was studied by mixing different amounts of organic carbon powder with the ash samples prior to glowing.

Figure 6: Outline of the equipment set-up



Explanations:
(1) inlet of cooling water, T=50°C
(2) outlet of cooling water
(3) inlet of purge gas (air or N_2)
(4) outlet of purge gas
(A) cold precipitation surface "cold finger"
(B) ceramic funnel with ash sample
(C) heated part of oven
(D) gas washing bottle
(E) gas flow meter
(F) temperature measurement

Table 2: Overview of the average concentrations [mg/kg ash (dry basis)] of important elements in the ashes investigated

Explanations: * the concentration of C_{comb} was calculated on the assumption that C is not removed with the eluate water

Element	ESP-G fly ash	ESP-G fly ash (leached in H_2O)	CS-G fly ash	ESP-CFB fly ash
		[mg/kg (d.b)]		
Cd	33	40	83	14
Pb	304	401	610	100
Zn	3,665	4,620	15,547	1,340
Cu	220	260	284	96
K	92,498	6,642	6,753	45,600
Na	5,453	1,738	1,035	18,200
S	44,824	15,586	12,374	22,000
Cl	9,480	658	265	14,800
Ca	280,417	340,908	245,000	196,000
Si	11,208	14,975	22,825	136,000
$C_{comb.}$	68,600	* 90,552	50,400	12,000
C_{CO2}	60,200	not analysed	199,450	51,000

The ash samples used for the experiments were completely digested and analysed for their content of: Al, As, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, P, Pb, S, Si, Zn, C_{comb} and CO_2 (carbonate). After every experiment the residual ashes as well as the dissolved precipitate from the cold finger, the solution from the gas washing bottle and the solution gained from washing the connecting quartz tubes were analysed for the elements As, Cd, Cl, Cu, K, Pb, S and Zn. All analyses were performed with special methods approved and tested in the Round Robin carried out at the beginning of the project [1].

In addition to wet chemical analyses of the condensed layers on the cold finger, dry samples of precipitate were collected on an adhesive graphite tape and analysed by means of scanning electron microscopy (SEM) in order to achieve a more comprehensive understanding of the chemical compounds and the formation of the condensed species.

Chemical and microbial treatment of heavy metal contaminated biomass ashes: chemical leaching, bioleaching and biosorption of heavy metals from leachates of biomass ashes

Chemical and biological leaching of heavy metals from biomass ashes (ESP fly ash and condensation sludge) from Austrian grate-fired biomass combustion plants was investigated. The fly ashes were the same samples also used in the thermal treatment experiments. Bioleaching was conducted using 2 subspecies of the fungus *Penicillium simplicissimum*. Since efficiency of microbial metal leaching depends on the ability of the microorganisms to become adapted to high concentrations of ash in the leach suspension, adaptation of fungi with increasing amounts of ashes was performed. With the adapted fungi four bioreactor test runs were conducted with two kinds of ash and two *Penicillium simplicissimum* subspecies with comparable bioleaching capacity.

The bioreactor consisted of a 2 l glass vessel provided with a stainless steel top plate with a central stirrer [11]. Samples were taken on a daily basis in order to investigate time-dependent leaching behaviour of heavy metals in a representative bioreactor test run. The solubilised heavy metals (Zn, Cu, Cr, Pb, As, Co, Ni, Co, Mo, and Hg) were determined by flame and graphite tube atomic absorption spectroscopy. Production of citric acid was determined by gas chromatography after derivatisation.

Since the leaching rates obtained with *Penicillium simplicissimum* in the one-step process were not high enough to be applicable on an industrial scale, a two-step process was conducted where citric acid as leaching agent was produced and excreted by *Penicillium simplicissimum* without contact with the ash. Moreover, a biochemical leaching process following a pre-leaching step with inorganic acids at a pH of approximately 7 to remove the alkalinity of the ashes was investigated.

Citric, lactic, oxalic, sulfuric and hydrochloric acids were employed in chemical leaching experiments. The results actually achieved by different leaching methods were compared to the aims of reduction calculated according to the guiding values specified for biomass ash utilization in forests and on agricultural fields, and according to the allowable concentrations in soils in Austria. In order to decide which acid was most economic for leaching purposes, the costs to extract 1 t of ash at 98-100 % w/v solubilisation efficiency for Cd and Zn were compared.

The final process scheme developed from the investigations performed, following the objective of heavy metal removal, consisted of the following steps:

- leaching of the heavy metal contaminated ashes with weak inorganic acids like sulfuric acid,
- precipitation of the leachates by raising the pH,
- sorption of heavy metals still remaining in the leachate by microbial sorbents.

Concerning the investigation of the biosorption process, an exhaustive survey and assessment of the microbiological literature on heavy metal biosorption led to the identification of 6 potentially suitable organisms [12, 13, 14, 15; 16;]. These organisms are the fungi *Cunnighamella blakesleeana, Rhizopus oryzae, Mucor plumbeus, Penicillium spp*., the yeast *Saccaromyces cerevisiae* and the bacterium *Bacillus megaterium* KM. All biomass samples were autoclaved, cleaned with deionised water, freeze-dried and ground prior to testing. Except as otherwise described, for all experiments, defined amounts of biosorbent fungal powder were contacted with 30 ml of metal nitrate solution (ph adjusted to 7) in a 50 ml polypropylene centrifuge tube that was then shaken in a rotary shaker. Contact time was approximately 24h, which is more than ample time for adsorption equilibrium [17]. Both chemical and physical pre-treatments were tested as means of enhancing the biomass loading capacity.

The biosorption of single species of heavy metals was studied in order to determine the optimum conditions for heavy metal removal of the leachates. At first, the ability of the biosorbents to remove single ions (Zn^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}) was investigated using the corresponding sulphates and chlorides, respectively. Subsequently, a solution containing two metals (Zn^{2+}, Ca^{2+}) was tested to ascertain the existence of possible interaction among ions or competition. Finally, biosorption experiments were carried out with the leachates obtained by chemical leaching of ashes and further precipitation [18]. The concentration of biomass in the experiments was up to 13 g/L dry weight. The release of heavy metals from the biosorbent was achieved by an inexpensive and simple reagent: hydrochloric acid [19].

For the characterisation and comparison of biosorbents the data obtained by the biosorption of single heavy metal ions at different initial concentrations were fitted to a Langmuir model [20]. In this way it is possible to establish the maximum load capacity of the biomass at the corresponding equilibrium concentrations. In addition to equilibrium studies, kinetics of biosorption were determined in order to establish the rate of metal uptake.

Both equilibrium and kinetic characterisations of the biosorbent material are crucial for process design.

Results and conclusions

Theoretical investigations and modelling of ash formation and heavy metal behaviour in biomass combustion and gasification processes

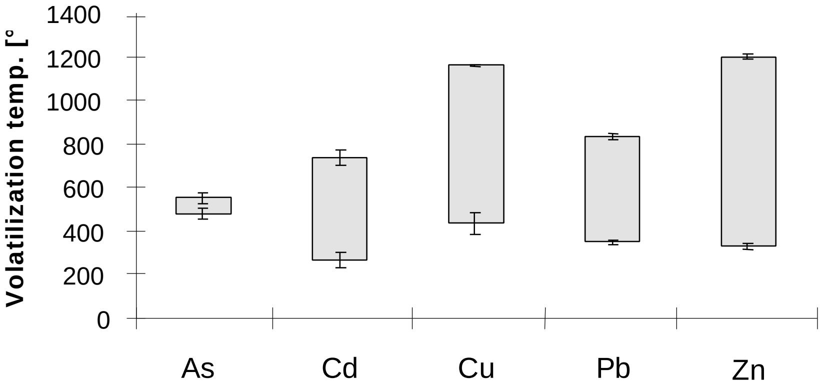
In order to be able to evaluate and explain results achieved from the different test runs and experiments performed within the project, existing codes and data for chemical equilibrium and models for particle formation were tested, evaluated and improved during the project. They should form the basis for simulating the behaviour of heavy metals during biomass combustion / gasification processes and evaluating relevant influencing variables.

Effects of fuel characteristics, combustion conditions and inaccuracies in thermochemical data on heavy metal volatilisation according to chemical equilibrium calculations

The volatilisation temperature (T50) is defined as the temperature at which 50 per cent of the specific element is in the gas phase. In order to determine the volatilisation temperature as a function of all variables, a sensitivity analysis was performed by utilising underlying fractional factorial designs to structure the chemical equilibrium calculations. The designs are mathematically optimal schemes in which all potentially important variables are changed systematically to maximise information while minimising the number of calculations required, thereby significantly facilitating the estimation of the desired effects [5].

The results from sensitivity analyses on chemical equilibrium model calculations of biomass combustion and gasification showed that volatilisation of As is mostly affected by the air-to-fuel ratio (λ), the amount of As in the fuel and the inaccuracy of the thermochemical data of As_2O_5 (c) and As_4O_6 (g). A higher value of Gibbs free energy for formation ($\Delta fG°$) of As_2O_5 (c) resulted in lower stability and, thus, a somewhat lower (25 °C) volatilisation temperature for As. A higher $\Delta fG°$ of the gaseous As_4O_6 slightly increases the volatilisation temperature. For Cd, Cu, Pb and Zn, the most influencing variables are the amounts of Cl, S and the specific metal in the fuel.

Figure 7: Variations in the volatilisation temperatures (T50) for As, Cd, Cu, Pb and Zn according to chemical equilibrium model calculations caused by fuel variables, operating conditions (hatched areas), as well as inaccuracies in thermochemical data (error bars).



The interaction terms between the amount of Cd, Cu, and Zn and the amount of Cl indicate that the effects on T50 of Cl increase with higher amounts of heavy metals. For these metals, the effects of uncertainties in thermochemical data were relatively small compared to the other effects, although for example the lower level of $\Delta fG°$ for Cu_3Cl_3 (g) in high Cl fuels may lower T50 by as much as 50 °C. The species with significant effects of uncertain data are: As_2O_5(s), As_4O_6(g), $CdCl_2$(g), $CdSO_4$(s), Cu_3Cl_3(g), PbCl(g), and $PbCl_2$(g). It should also be noted that PbCl4(g) was excluded from the calculations owing to unrealistic effects at low temperatures. Due to this fact it is recommended to be careful using the JANAF data for $PbCl_4$(g).The inaccuracies in thermochemical data resulted in maximum effects of 25, 35, 5-52, 12, and 1 °C for As, Cd, Cu, Pb and Zn, respectively. These results are generally in good qualitative agreement with controlled experimental data recently reported by Jakob et al [21 22], although for municipal solid waste ash.

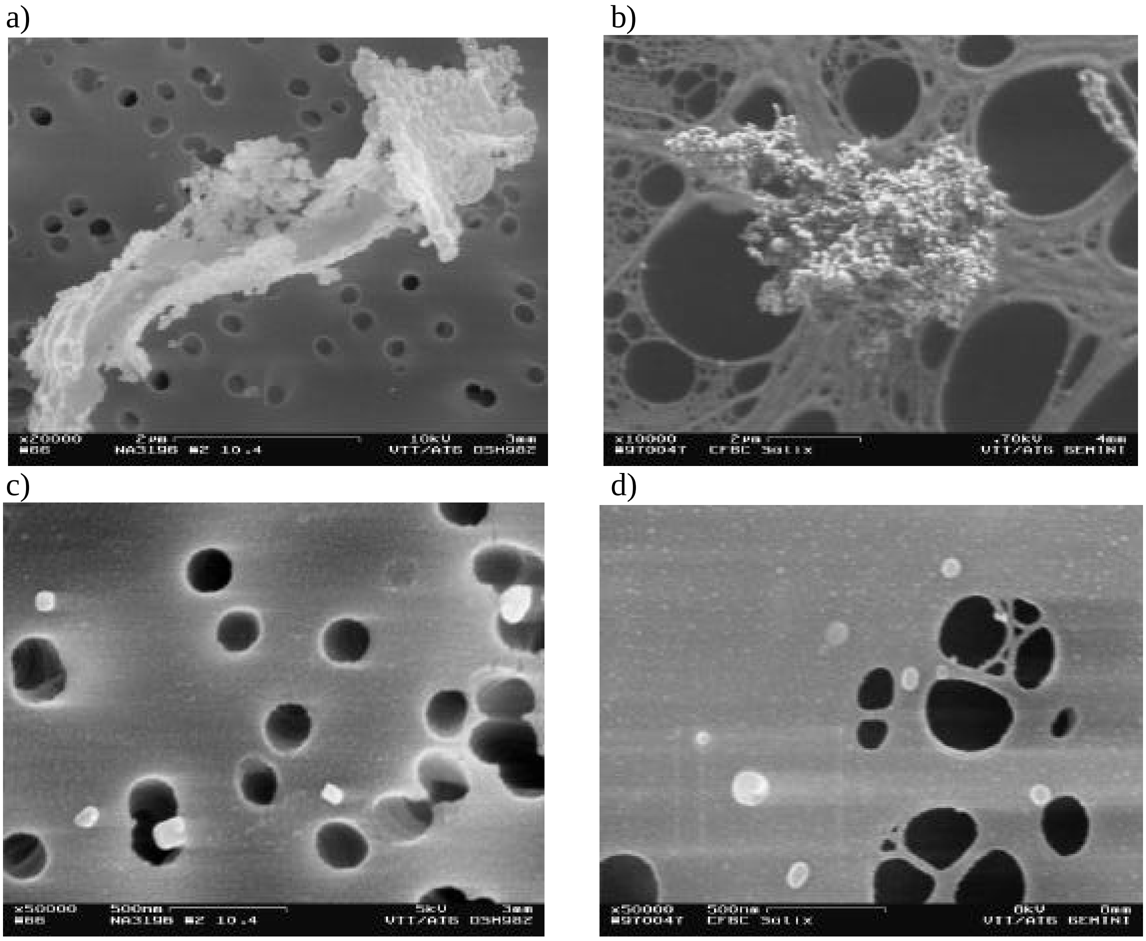
Thus, the results indicate that a significant separation of As, Cd and Pb should be expected for any fuel combination and operating condition taking into consideration that the temperature in biomass furnaces is in the range of 800-1,000°C. The volatilisation temperatures of Cu and Zn are higher and more clearly influenced by the elemental characteristics of the feedstock. Fuel mixing could therefore be a cost-effective measure to increase volatilisation and thereby separation of these elements from the bulk ash.

Aerosol modelling in CFB combustion and gasification of biomass

The gas-to-particle conversion mechanisms of the vapours onto the surfaces of spherical particles have been well-described in the literature [23]. However, by studying the morphology of fly ash from the CFBC experiments carried out in this project with scanning electron microscopy (SEM), VTT found out that coarse mode (D_p > 1 µm) fly ash particles were agglomerates consisting of up to thousands of submicron-sized primary particles. (see Figure 8)

Figure 8: **SEM micrographs of the fly ash particles formed during CFB combustion of forest residues (a and c) and willow (b and d).**

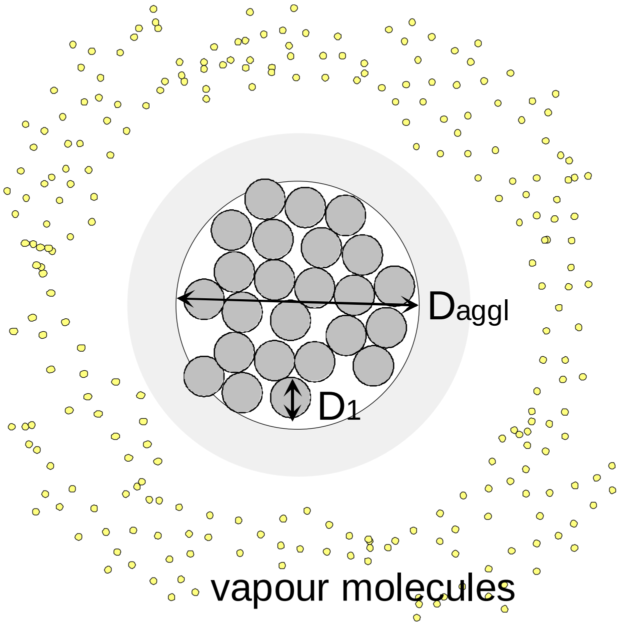
Explanations: The coarse fly ash particles were agglomerates (a and b), and fine fly ash particles mostly single spherical or slightly rectangular shapes (c and d).



The primary particles with varying compositions had partially molten and sintered together to agglomerates. The coarse fly ash particles had been presumably formed inside and on the surface of the burning char particles from the ash-forming species which did not volatilise during combustion. In pulverised coal combustion, these ‘residual ash’ particles are mainly spherical, formed from molten ash species. Clearly, the morphology of the residual ash particles from CFBC of biomass is completely different from the morphology of the residual ash particles from pulverised coal combustion.

For this reason, equations which are valid for spherical particles could not be used for the fly ash particles formed during CFB combustion of forest residues and willow. Therefore, a conceptual aerosol model was developed to describe the fly ash particles as fractal-like structures [24]. In the model, the particles are assumed to be agglomerates consisting of spherical primary particles with a uniform size with a diameter D_1. The diameter of the sphere closing the agglomerate is D_{aggl}, (see Figure 9). The diameter D_{aggl} is defined as the aerodynamic diameter of the agglomerate if experimental results are used as input.

Figure 9. Schematic figure of an agglomerate particle with primary particle diameter D_1 and overall agglomerate diameter D_{aggl}.



Based on the agglomerate model, the dependence of the concentration of the volatilised species on the agglomerate diameter was derived for different gas-to-particle conversion mechanisms. Primary particle size D_1 and fractional dimension R_f of the particles was assumed constant for all the particles. In the continuum regime, i.e. gas mean free path λ much smaller than the particle diameter D_{aggl}, condensation or a fast chemical reaction were found to result in the concentration m_i/m_{tot} dependence on agglomerate diameter D_{aggl}:

$$\frac{m_i}{m_{tot}} \propto \left(D_{aggl}\right)^{1-R_f}$$ **Equation 3**

The concentration of the volatilised species was found to be independent of the agglomerate diameter, only depending on the primary particle surface area A_1 and volume V_1 if gas-to-particle conversion occurred by a slow chemical reaction:

$$\frac{m_i}{m_{tot}} \propto \frac{A_1}{V_1} \quad \text{for all values of } D_{agg}$$ **Equation 4**

Material fluxes and fractionation of heavy metals in biomass CFB combustion plants

A full-scale one-week CFBC test run was performed by VAT in April 1996 at the CHP plant in Nässjö. During the first test period forest residues and during the second test period willow (*Salix*) were used as fuels.

The operating conditions were stable during the test runs, average values of the recorded operational data are presented in Table 3.

Due to the fact that it was impossible to weigh the amount of fuel fed to the furnace this value was instead calculated from the energy balance of the plant and the NCV (net calorific value) of the fuel achieved from analyses. In this way the amount of ash fed to the plant with the fuel was also obtained. The amount of ash leaving the plant was measured by weighing ash containers before and after the test periods.

During the measurements large amounts of fly ash deposited in the convective section of the boiler and, as no soot blowing was done during the test periods, differences between ash in- and output in the boiler section were considerable. In order to overcome this problem results from aerosol measurement performed by VTT upstream and downstream the convective pass were used to estimate the amount of fly ash deposited. The calculated mass flows through the plant are displayed in Table 4.

Table 3: Recorded operational data during measurements at the Nässjö kraftvärmevärk

	CFBC of forest residues	CFBC of *Salix*
Boiler load (% of full load)	80	70
Heat effect (MW)	16	14.1
Electric effect (MW)	7	5.5 - 6
Heat effect from flue gas condenser (MW)	---	4.3 - 5
Bed temperature (°C)	780	780 ± 20
Temperature at the top of the furnace (°C)	880	870 ± 10
Total airflow (Nm^3/s)	8.3	8.4
NO (ppm)	84	70
SO_2 (ppm)	7.0	11
CO (ppm)	3-512	0-500

Table 4: Mass balance data for fuel and ash fractions

	CFBC of forest residues	CFBC of *Salix*
Fuel (kg/h)	5,475	5,013
Ash from fuel (kg/h)	115	80
Bed material (kg/h)	239	53
Bottom ash (kg/h)	283	92
Filter fly ash (kg/h)	44	23
Difference between incoming and outgoing ash +bed material (kg/h)	27	18
Deviation (%)	8	14

Mass balances for ash matrix elements (Ca, Mg, Na, Si, K, P), S, Cl and the heavy metals Cd, Pb, Cu and Zn were calculated by combining aerosol measurements upstream of the convective pass with fuel, bottom, and ESP ash analyses. The mass balances were then used to calculate the fraction of each element that was removed from the furnace with the bottom ash.

24-27 % of the total ash was removed from the furnace with the bottom ash during combustion of forest residues, and approximately 22-37 % during combustion of willow (*Salix*). For both fuels chlorine and cadmium were almost non-existent in the bottom ash, and sulphur clearly depleted (see Figure 10 and Figure 11). This indicates that these elements were fairly volatile and got enriched in the fly ash. Potassium and zinc, on the other hand, were enriched in the bottom ash and hence depleted in the fly ash.

Despite the corrections above using the aerosol measurements, the mass balances did not close well, which is indicated in Figure 10 and Figure 11 by the amount of elements retained.

During combustion of forest residues between 65 and 80% of the heavy metals entering the plant with fuel and bed material could be found in the different ash fractions. During the combustion of *Salix* only 10% of the Cd could be found, mainly in the fly ash. The corresponding figure for Pb, Zn and Cu varied between 30 to 50%. The worse results for the *Salix* test runs can be explained by the fact that no equilibrium between bed material and ash could be achieved during the test runs, which means that certain amounts of elements accumulated in the bed during the experiments

Figure 10: Elemental mass balances during combustion of forest residues.

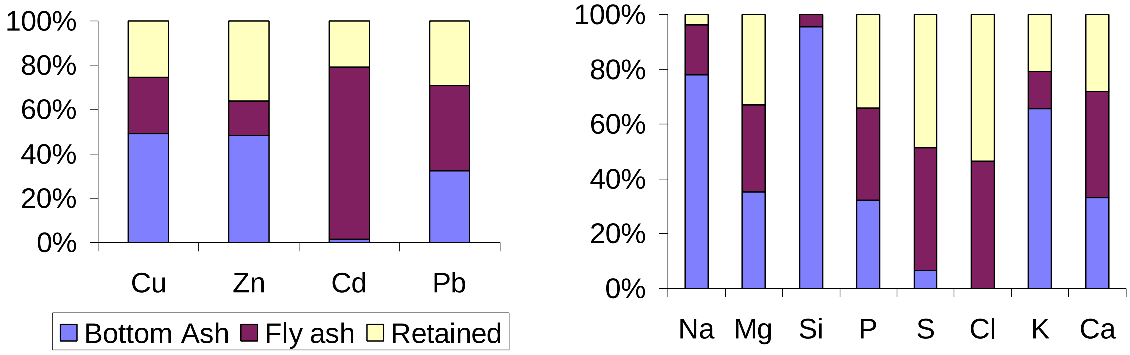
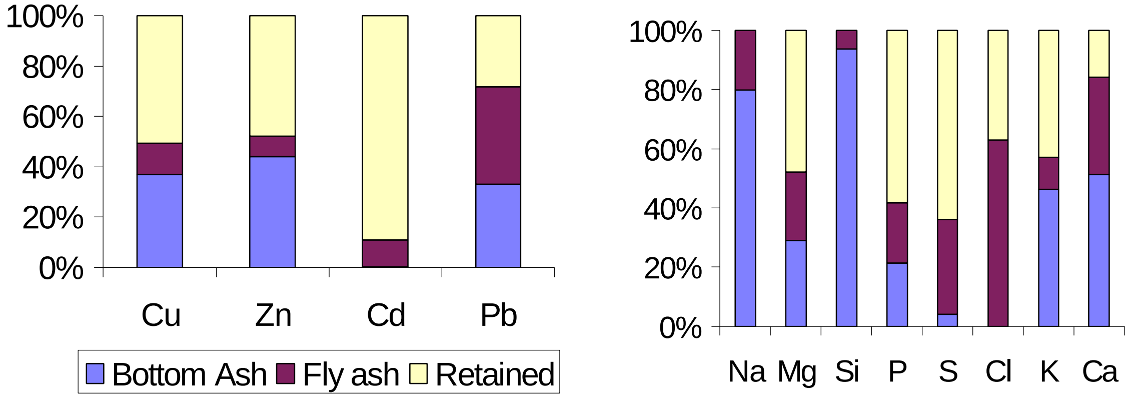


Figure 11: Elemental mass balances during combustion of *Salix*.



The morphology of the bottom ash was studied with scanning electron microscopy (SEM) by VTT. It was found that the ash was retained in the bottom ash by two different mechanisms: i) non-volatile species, e.g. calcium and silica, were attached to the bed particles as particles forming a porous ash layer on the bed particle surface, whereas ii) volatile compounds, e.g. potassium, were diffused into the bed sand matrix forming a potassium-silicate layer inside the sand particle. In some cases, the potassium-silicate layer filled the whole sand particle.

Mass size distributions of fly ash particles from CFBC of biomass

The mass size distributions of fly ash particles upstream and downstream of the convective pass were clearly bimodal with submicron modes at approximately D_p=100 nm at T=830°C and at approximately D_p=200 nm at T=150°C with forest residues. With willow, the submicron particle mode was found at 200-300 nm at both locations. The mass concentrations of the submicron modes with forest residues were 14-23 mg/Nm^3 (2 % of the total mass) and 23-25 mg/Nm^3 (4-10 % of the total mass) at 830°C and 150°C, respectively. With willow, the fine mode concentrations were 42-73 mg/Nm^3 (8 % of the total mass) and 36-68 mg/Nm^3 (19-25 % of the total mass) at 830°C and 150°C, respectively. The main compounds in the submicron modes were K and Cl with forest residues, and K and S with willow. The particle size distributions determined upstream of the convective pass had the major mode at approximately 15 µm during combustion of forest residues, and at around 7-8 µm during combustion of willow. Particles larger than about 10 µm were almost absent in the particle size distributions downstream of the convective pass section due to deposition of the fly ash particles in the convective pass in the absence of soot blowing [25; 26; 27]. The total particle mass concentration at 830°C was 920-1,300 mg/Nm^3 with forest residues, and 530-630 mg/Nm^3 with willow. Deposition in the convective pass was approximately 60-80 % of the total fly ash. The total particle mass concentration was higher and the submicron particle concentration lower with forest residues than with willow.

Behaviour of heavy metals in CFBC of biomass

All the heavy metals investigated were effectively captured by the coarse fly ash particles. The concentrations of the heavy metals downstream of the convective pass at 150°C did not show any enrichment in the fine particles. In fact, the concentrations were relatively size independent in the size range D_p>0.5 µm, and even decreased with decreasing particle size in the smaller particle size range [28; 29].

The behaviour of Cd, Pb and Zn was similar for both fuels. Cd was volatile in the bed, and it was found mainly in the coarse fly ash particles at the measurement location upstream the convective pass. The occurrence in the coarse fly ash particles was found to be due to a chemical reaction of volatile Cd species with the coarse fly ash particles. Pb was found to be at least partially volatile during combustion. 15-27 % of lead was found in the fine mode particles and in the gas phase at T=810-830°C. At least this fraction was volatilised during combustion. In the convective pass, the volatilised fraction reacted with coarse fly ash particles, and only minor amounts of Pb were found in the fine mode particles downstream of the convective pass. Zn was clearly enriched in the bottom ash with both fuels. The enrichment was presumably due to a reaction of volatile Zn with the quartz sand particles or the ash layer on the surface of the sand particles. Less than 3 % of Zn was found in the fine fly ash particles upstream of the convective pass. Only Cu behaviour was different with the two fuels. 24-27 % of copper was found in the gas phase at 830°C during the combustion of forest residues, but only approximately 2 % during willow combustion. Based on these results it is not possible to determine whether the marked copper occurrence in the coarse fly ash particles was due to a non-volatile behaviour, or a chemical surface reaction of volatile Cu with the coarse fly ash particles.

Speciation of Cd and Zn in fly ash from CFBC of biomass

XAFS analysis showed that the most probable Cd species in the fly ash from CFB combustion of willow were cadmium sulphate ($3CdSO_4 \bullet 8H_2O$) and Cd silicate ($CdSiO_3$). Earlier studies showed that Cd in biomass fly ash is not readily water soluble but can be easily dissolved in acids [30]. Cadmium sulphate ($CdSO_4 \bullet 8H_2O$), however, is very soluble in water [31]. This would indicate that Cd was not present as a pure cadmium sulphate in the fly ash samples from combustion of willow and that $CdSiO_3$ would be the more likely species. However, other sulphates and silicates of Cd are possible forms of occurrence of Cd in the fly ash samples as well. Based on the XAFS analysis, the existence of Cd as a chloride, sulphide or in metallic form can be excluded.

XAFS spectral structure of Zn indicated that ZnO was a significant component in the samples. However, the spectral data were different from the bulk ZnO, and it is probable that ZnO was present as very fine particles (< 30 Å) or as a very thin coating on the particles. The presence of zinc in the fly ash samples from the combustion of willow as very fine particles or a very thin coating on the particles was consistent with the other results. The enrichment of zinc in the bed and the occurrence of zinc in the coarse fly ash particles could be a result of a surface reaction of zinc with the bed particles and with the coarse fly ash fraction. The XAFS analysis findings that Zn was found as a thin layer on the fly ash particles confirms that zinc volatilised during combustion and ended up in the coarse fly ash fraction by a surface reaction or adsorption of the gas phase zinc compounds forming a thin ZnO layer on the fly ash particles. Accordingly, the enrichment of zinc in the bottom ash was presumably a consequence of diffusion of gas phase zinc compounds into the bed particles.

Chemical equilibrium model calculations in comparison with experimental results from CFBC of biomass

In oxidising environments ($\lambda > 1$), cadmium, lead and zinc from both forest residues and *Salix,* were predicted to behave similarly. Cadmium and lead are both predicted to be in the gas phase (> 700 and 600°C) in the main part of the furnace, while Zn is predicted to be solid as ZnO up to 1,170°C. No complex compounds of these three elements were found stable while considering the bed material as inert to reactions with the heavy metals.

In contrast to the predictions for Cd, Pb and Zn with the introduced complex compounds, arsenic is likely to form calcium or alkali arsenates in oxidising atmospheres, where the calcium arsenate is very stable up to above 1,050°C. If kinetically inhibited, alkali arsenates may also form in the whole temperature range, but the thermochemical data for these compounds are extrapolated above 700°C, which imposes considerable uncertainties. Copper will preferably form copper aluminate up to above 1200°C in oxidising atmospheres.

As discussed in previous work [32], the fractions of chlorine and sulphur that are actually available for reactions with the heavy metals are crucial for the exact condensation temperatures, except for As. The general results in the present work originate from calculations including all major ash-forming elements, and thus represent a “worst case scenario” with respect to condensation temperatures. By including all alkali to capture a maximum of chlorine, the highest possible condensation temperatures of the heavy metals are obtained. By assuming that some of the chlorine theoretically expected to form alkali chlorides would not have time to fully react, results with somewhat lower condensation temperatures are obtained.

In the reducing conditions in the fuel particles and below the secondary air inlets, the same behaviour was obtained for the two fuels, but significantly lower volatilisation temperatures were predicted. As, Cd and Pb are all in the gas phase at a temeperature of 500°C or higher. Zn and Cu volatilise from 600 to 700 and 950 to 1050°C, respectively. This would imply that all the heavy metals of concern, except Cu, would initially be in the gas phase under the conditions studied. At lower temperatures, the stable condensed species were predicted to be potassium arsenate, CdO or CdS, Cu_2S, PbS, and ZnS.

It should also be noted that the SiO_2 in the bed material was assumed to be inert throughout the calculations and was thus not considered. Based on the results from analysing the spent bed material, this assumption seems to be definitely warranted for Cd, but further studies are needed to explicitly exclude any potential interactions between bed material and the other metals.

In contrast to the calculated distributions, the experimental results clearly indicated that, although Cd and Pb probably both are volatilised initially, they are found in condensed forms associated with the larger ash agglomerates downstream of the cyclone at about 830°C. The elemental balances also showed that these metals are enriched in the cyclone ash. Some additional compounds or solutions must therefore be responsible for the capture mechanism for Cd and Pb. The experimental distribution of Zn, on the other hand, showed a qualitative agreement with the predictions. Because of the general ash retention in the bed and significant fractionation of the different major ash components within the plant, it is not easy to draw any further conclusions from the comparison.

Fractionation of heavy metals in bench-scale isothermal bubbling fluidised-bed combustion experiments

The effects of temperature, together with more and less reducing conditions in the bed, on heavy metal fractionation were determined under controlled and isothermal conditions using the same fuels from the large-scale CFBC test runs performed by VAT.
However, despite the better control of the process in the bench-scale equipment compared to the full-scale plant, similar problems with closing the elemental mass balances occurred. This was mainly because of the (i) small sample sizes of the filter ashes that could be obtained within reasonable experimental times, (ii) potential loss of material deposited/condensed in the furnace and sampling probes and, most importantly, (iii) uncertainties of the actual fraction of the total material introduced into the sample cyclone placed in the hot flue gases. Although a calibration of the gas flow through the cyclone was performed before every experiment (about 10 % deviation), continuos build-up of a filter cake on the filter placed downstream the cyclone probably altered slightly during the experiments.
The fractionation distributions of each of the specific metals (Cd, Cu, Pb, Zn and K) are therefore described by comparing the raw data of the concentrations in the different materials. The distribution results from chemical equilibrium model calculations are the same as for the large-scale test runs because the same fuels were used.

Cadmium – Based on the raw measured concentration data, cadmium from both fuels was found to be somewhat enriched in the filter ash. Relatively much of the Cd from *Salix* is still contained in the cyclone ash, and no other obvious trends with the studied variables can be identified. However, for the forest residues, a significant increase of the Cd in the filter ash with increasing temperature was observed. This is in qualitative agreement with the chemical equilibrium results, although potentially at a somewhat higher temperature than predicted.

Copper - In spite of the values below the detection limit (<10 ppm) for the bed ash concentrations for *Salix*, and corresponding relatively low concentrations for forest residues, multiplication by the respective weights indicate a large fraction of Cu to be retained in the bed ash. The general characteristics of the Cu data are, however, the large variations and the absence of obvious trends, with considerable amounts in the cyclone ash for *Salix* as fuel.

Lead - In agreement with the equilibrium predictions and the results for Cd, Pb is somewhat enriched in the filter ash. There is also a small indication as to higher amounts in the filter ash with increasing temperature.

Zinc - A relatively large fraction of Zn was retained in the bed material, although a significant enrichment in the filter fly ash compared to the cyclone ash was obtained at the highest temperature. This potentially indicates that Zn initially volatilises under reducing conditions in the bed and fuel particles and subsequently undergoes a homogeneous condensation to ZnO at high temperatures.

Potassium - In addition to a likely significant capture in the bed material, a large fraction of K seems to exit the furnace in gas phase, and K is thereby enriched in the filter ash.

Because of the relatively large amount of material, and the low concentrations measured often below the detection limits (except Zn) no conclusions could be drawn about potential enrichments or depletions of heavy metals in the bed material. Further work is needed to determine the actual retention of Cd, Cu and Pb in the bed, as well as for future total closure of the elemental balances.

Fractionation of heavy metals in biomass CFB gasification plants

In October 1997, a one-week test period in a CFB bark gasifier was carried out by VAT at Värö bruk in Sweden. The testing comprised three test runs, lasting 8, 11 and 4 hours, respectively. The operating conditions were stable during each test run and the average operational data are displayed in Table 5.

Due to technical problems it was not possible to measure the amount of fuel fed to the plant, and since the heat from the plant is only used internally the heat produced is not registered. Therefore, the calculation procedures applied in the course of the CFBC test runs could not be used. Furthermore, the fly ash produced during the gasification process is not separated after the reactor, but accompanies the gas into the lime kiln and the fuel drier. Therefore, it was not possible to weigh or sample the ash produced according to the procedures developed for the CFBC test runs. Instead, data from aerosol measurements performed by VTT were used for estimating the amounts and composition of the fly ash. The turnover of bed material was measured and bottom ash samples were analysed although the amount of bottom ash produced was impossible to measure due to disturbance by an unknown amount of water added to the ash.

As a consequence of the problems concerning the recording of the basic parameters mentioned above, the parameters had to be estimated. Basically, this was done by using the measured fuel gas composition of (CO, CO_2 and hydrocarbons) and a gasification model. The water, H_2 and tar content of the fuel gas was calculated from the model and further used for establishing energy and mass balances which subsequently yielded the mass flows through the plant (see Table 6). By considering all the estimations performed, the deviation of 19% in the experimental mass balance was satisfactory.

Table 5: Recorded average operational data during measurements at the Värö bruk CFB bark gasifier.

Operational data	CFBG of bark
boiler load (% of full load)	55-70 %
bed temperature	800 °C
temperature at the top of gasifier	740 °C
conc. CO in flue gas	9 %
conc. CO_2 in flue gas	20 %
conc. hydrocarbons in flue gas	2,000-2,600 ppm

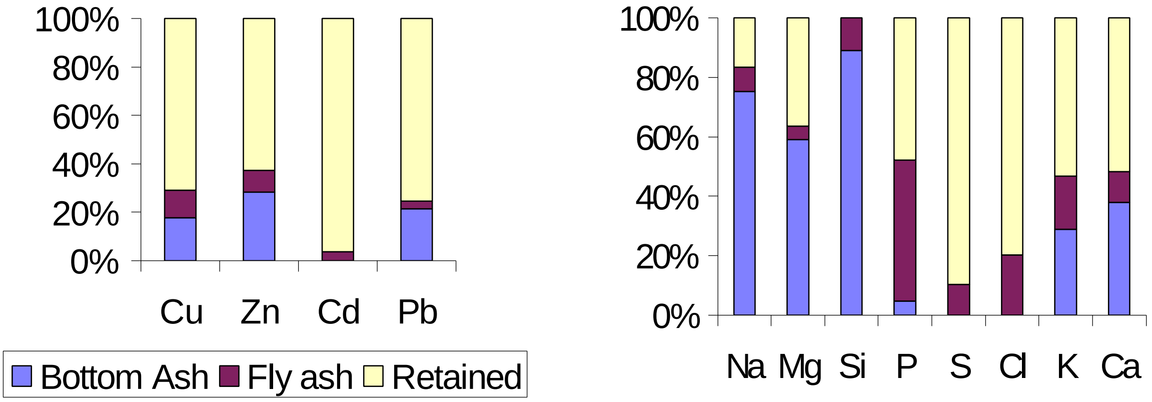
Table 6: Experimental mass balance from the measurements at the Värö bruk CFB gasifier.

Mass flows at CFBG of bark	(kg/h)
calculated fuel feed	3,485
ash from fuel (in)	186
bed material (in)	160
bottom ash (out)	161
fly ash (out)	120
difference between incoming and outgoing mass flows	65
deviation (%)	19 %

Factors, such as the uncertain water content of the bottom ash and the very high and varying amount of unburned char in the fly ash samples, disturbed the elemental analyses considerably. Consequently, the rates of recovery for the different elements investigated varied significantly (see Figure 12).

Only 3% of the Cd could be found in the ash, the corresponding figures for Pb, Zn and Cu being 30 - 40%. With the exception of Si, generally smaller amounts of elements were found in the outgoing streams of ashes compared to the incoming streams of fuel and bed material. Furthermore, it is worth noticing that no Cd was found in the bottom ash.

Figure 12: Elemental mass balances during gasification of bark at the Värö bruk



Mass size distributions of fly ash particles from CFB gasification of bark

The fly ash particle concentrations during CFB gasification were 60-80 g/Nm^3. The fly ash contained unburned char in addition to ash particles. The fly ash particle size distributions were found to be bimodal during CFB gasification of bark with fine mode at D_p= 0.7 μm and coarse mode at D_p= 25 μm. The unburned char content in the coarse mode particles was approximately 75 %. The tar content in the fine mode particles was highest in the fine particles with up to 90 % of the particles of 0.5 μm consisting of tars, and lowest for particles of 1-2 μm. Less than 3 % of the ash was in the particles smaller than about 2 μm.

Heavy metal behaviour in CFB gasification of bark

The major fraction of all heavy metals investigated - Cd, Pb, Cu and Zn - was found in the coarse particle fraction at both measurement locations at T=720°C and T=640°C. Less than 2 % of Cd, 8 % of Pb and 10 % of Zn were found in the particles smaller than 2 μm, indicating that the major fractions of these metals were not volatile during gasification or were adsorbed in the char before the measurement took place. Adsorption of heavy metals, especially mercury, in activated carbon has been observed in several studies, but it usually occurs at lower temperatures (300-500K) and the adsorption efficiency has been observed to decrease with increasing temperature. Therefore, adsorption of the heavy metal vapours in the residual char at temperatures around 700°C is not likely. It is more likely that the binding of the major fraction of Cd, Pb and Zn in the coarse fly ash fraction resulted from the non-volatile behaviour of the heavy metals or from a chemical surface reaction of the heavy metals with the ash compounds.

Chemical equilibrium model calculations of CFB gasification processes compared to experimental results

In contrast to the experimental results, chemical equilibrium distributions between condensed and gaseous forms for the gasification tests indicated that all heavy metals except Cu should be in the gas phase at temperatures above 700°C, as the bed, top and sampling temperatures of the gasifier were 800, 740 and 730°C, respectively. However, depending on the speciation, the same compounds found in combustion test runs could potentially retain Cd, Pb and Zn also at gasification conditions, which is supported by the preliminary results from the experiments. It can also be noted that the critical equilibrium temperature for condensation of Cu is significantly lower than in combustion atmospheres.

Fractionation of heavy metals in grate-fired biomass combustion plants

In the Danish part of the project, a total of 4 full-scale test runs on straw-fired boiler systems were performed, one of which was an additional experiment financed by SK-Power, a Danish utility company. Another 3 full-scale test runs on forest wood chip-fired systems were financed solely by the Danish Energy Agency. The experiments were aimed at giving general figures for trace element fractionation in ashes, providing further understanding on the processes influencing fractionation especially in the combustion zone, and making available general figures on the mass of each ash fraction.
Average operational parameters for the test runs and the average values are shown in Table 7.

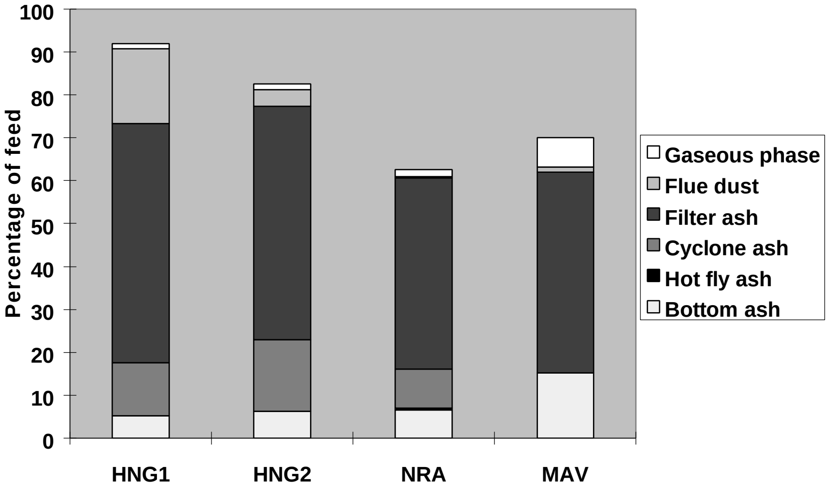
Table 7: Mass balances and average operating data for the Danish full-scale experiments in grate-fired straw combustion plants

	Ash balance [%]	Oxygen [%]	CO [ppm]	Furnace temp. [°C]
Høng1	99	10.1	1,607	858
Høng2	87	7.9	1,931	859
Nr. Aslev	97	8.3	2,666	654
Masnedø	77	4.5	376	939

Although the investigation covered a wide range of metals, the main focus was placed on cadmium, which is the trace element that most often poses problems in ash recycling.
Figure 13 shows the percentage of cadmium in fuel feed found in the different ash fractions in the four experiments on straw-fired plants.

Figure 13 Mass balances for cadmium at the full-scale experiments in the straw combustion plants Høng and Nr.Aslev as well as in the CHP plant Masnedø

<u>Explanations:</u> Experiments in Høng (HNG1 and HNG2), Nr. Alslev (NRA) and Masnedø (MAV) show how cadmium in straw feed is fractionated between bottom ash, hot fly ash after the furnace (Nr. Alslev only), cyclone ash, bag filter ash (in Masnedø however the filter ash is ESP ash mixed with cyclone ash), in the flue gas as dust and in the gas phase.



The amount of cadmium between the top of the columns and the 100-percent mark represents material accumulated as deposits and potential accumulation of ashes in ash transport systems etc. during the experiments as well as uncertainties from weighing, concentration figures from laboratory analyses etc.

The greater part of cadmium in the straw experiments is found in the bag filter ash (in Masnedø in the mixed ESP and cyclone ash). This ash fraction typically accounts for only about 15 to 25 percent of the total ash amount.

Behaviour of heavy metals in straw-fired grate combustion plants

No aerosol measurements were performed during the test runs in grate combustion plants in Denmark within this project. However, by combining results from different ash fractions collected by DKT with SEM micrographs of fly ash particles from grate combustion units provided by TUG and the results of aerosol measurements in straw-fired grate furnaces from Christensen [33], a qualitative analysis of the behaviour of heavy metals in biomass grate combustion plants was performed by VTT.

The ashes collected by DKT were collected from different locations in the Danish boilers and categorised in ‘hot ashes’, precipitated at temperatures >630°C, i.e. bottom ash and hot fly ash, and ‘cold ashes’, precipitated at temperatures between 120 and 150°C, i.e. cyclone ash, filter ash and flue dust. The major difference between the different cold ashes was their particle size: cyclone-collected particles are larger than 2 µm, filter-collected particles, which have passed through the cyclone, are generally smaller than 2 µm. Flue dust particles are even smaller than filter fly ash particles, the average size being less than 1µm.

According to the SEM micrographs from Austrian grate combustion units, the coarse fly ash seemed to be formed of i) large molten particles with diameters between 10 and 100 µm, and ii) agglomerates consisting of submicron-sized primary particles with a typical size range smaller than 0.5µm. The coarse and molten fly ash particles were also covered with agglomerates.

In the section ‘Aerosol modelling’ in this report, VTT presented a gas-to-particle conversion mechanism of the volatilised heavy metals and the resulting dependence of the heavy metal concentrations on the particle size. For spherical particles, both condensation and chemical reaction should result in concentrations of the aerosols in the fly ash increasing with decreasing particle size. For the agglomerates, the concentrations also increase with decreasing particle size in the case of condensation, whereas in the case of a slow chemical reaction the concentrations are independent of the particle size. The particle morphology of coarse fly ash particles according to the SEM micrographs provided by TUG and Christensen [33] seemed to be somewhere between the morphology of the residual ash from pulverised coal combustion, where residual ash particles are spherical, and fluidised bed combustion fly ash, which solely consists of agglomerates. Consequently, the concentration resulting from a slow chemical surface reaction probably increases with decreasing particle size, but the increase is smaller than $1/D_p$ as predicted for spherical particles. Due to the higher combustion temperatures in grate-fired combustion plants in comparison to CFBC the amount of molten particles is dominant in the coarse fly ash fraction. A further difference to CFBC is the fact that no bed material interactions are possible in grate-fired units. Thirdly, due to the molten structure of coarse fly ash particles (with their comparatively small surface area), metal vapour condensation or reaction with fine fly ash particles (having a large surface area) is of major importance.

In the following, the behaviour of different elements in grate-fired biomass combustion plants is described based on the available results.

Cadmium. Cd is depleted in the hot ashes (bottom ash and “hot fly ash”) indicating volatilisation. Its concentration in the cold ashes increases with decreasing particle size. XAFS analysis indicated that Cd is most probably present as $CdSiO_4$ or $CdSO_4$ in the filter ash. At temperatures below 950°C surface reactions of Cd with silicates, sulphates or aluminosilicates gain importance. With increasing temperature of combustion these surface reactions are supported ($T > 950°C$), which means that Cd remains in the gas phase at high temperatures.
This, together with the Cd concentration being relatively independent of particle size, would suggest that Cd volatilises in the reducing atmosphere on the grate, and subsequently, reacts with the silicates or sulphates in the fly ash.

Zinc. The Zn is depleted in the bottom ash, and Zn concentration also increases with decreasing fly ash particle size. XAFS analyses showed that Zn can be present as ZnO or as Zn^{2+} bound in four-fold co-ordination by oxygen (for instance Zn_2SiO_4, Zn_2FO_4 or Zn-aluminosilicate). This means that both condensation and surface reactions are likely to occur concerning Zn behaviour in grate-fired biomass combustion plants.

Lead. Pb, like Cd and Zn, is depleted in the bottom ash and enriched in fly ash particles. Moreover, Pb concentration in filter fly ash particles increases with decreasing particle size. Since aerosol studies have shown that Pb reacts with silicates, these reactions are assumed to be of importance in the Si-rich straw ash. On the other hand, a considerable part of Pb seems to volatilise during combustion and is then bound by surface reaction to the fly ash particles. This process would again be dominated by Pb silicate formation.

Potassium. K concentration is lower in the bottom ash and hot fly ash than in the cyclone or the filter fly ash. According to XRD, K was mostly present in the fly ash as KCl and K_2SO_4. These compounds condensed on the fine fly ash particles. In the bottom ash and the hot precipitated fly ash, K was presumably present as K silicates formed by a reaction of volatilised K with silicates. Si concentrations in the samples were not analysed, but typically, the Si content in the straw is significant. Some K_2SO_4 may also have been found in the hot ashes.

Calcium. Ca was clearly depleted in the fine fly ash particles and its concentration in the other ashes was fairly constant. Presumably, Ca did not volatilise during combustion. The depletion in the fine fly ash particles is due to the enrichment of K, S and Cl in these particles.

Sulphur. S was slightly depleted in the hot ashes indicating volatilisation and was consequently enriched in the fly ash particles (mainly forming alkali sulphates), and partly also remains in the gas phase as SO_2 or SO_3.

Chlorine. Cl was clearly depleted in the bottom ash indicating volatilisation. It was already present in the hot fly ash. Alkali chlorides, mainly KCl, are formed and condensate on fine fly ash particles. Part of the Cl is also likely to remain in the gas phase as HCl.

Chemical equilibrium model calculations compared to experimental results for grate combustion of straw

The different equilibrium distribution diagrams for the different straw fuels and plants at oxidising conditions were very similar to the distributions predicted for forest residues and *Salix*. The small differences occurring for oxidising conditions can be directly related to the different Cl-to-K ratio, with additional influence of the sulphur content.

The results of the combustion test runs also showed that, by including potential formation of silicates, aluminates, ferrites, and calcium arsenate, several different calcium silicates were preferably formed from the silica. Aluminium was found to form calcium aluminates, iron calcium ferrite, and calcium also phosphates or silicates. Due to the large formation of these compounds no complex heavy metal compounds were found to be stable in the calculations.

The main experimental results were in qualitative agreement with the results from the CFB. The bottom ash was depleted in Cd, but enriched in Cu. Pb was found to be mainly equally distributed between the bottom ash and the filter ash, with some 15 percent in the cyclone ash. About 60 % of the recovered Zn were found in the filter ash. Although most of the metals maybe are volatilising, also the Danish experience was that a sophisticated in-furnace separation at the highest combustion temperatures probably is needed to avoid condensation.

Results and conclusions from Austrian bark and wood chip-fired grate combustion plants

Results from test runs performed by TUG within a national Austrian research project on fractionation of heavy metals in grate-fired combustion plants [2] were implemented in the evaluation of results from this EU project. The Austrian test runs, which comprised combustion of bark and wood chips, revealed a high potential of fractionated heavy metal separation in grate-fired biomass combustion plants. These results are in good agreement with results achieved from the test runs in Danish straw-fired grate combustion plants. Several individual elements were investigated but focus was put on the environmentally most relevant elements for Austrian conditions: Cd and Zn.

Depending on where the ash precipitation takes place within the combustion plant the following three influencing variables were found to be of significance (see Table 8): the gaseous atmosphere around ash particles, the temperature of ash precipitation, and the size of the fly ash particles.

The concentrations of Cd and Zn in the ash at high temperatures depend on the reduction potential of the gaseous atmosphere around the ash particles.

In a reducing atmosphere and at high temperatures almost the entire amount of Cd and Zn is volatilised, mainly as Cd(g) and Zn(g). Consequently, in order to reduce the concentration of heavy metals in the bottom ash, the temperature on the grate and in the primary combustion zone should be high and the primary air ratio under-stoichiometric.

High-temperature fly ash precipitation is costly and only effective for Cd but not for Zn fractionation due to adsorption and surface reactions of Zn vapours with the coarse fly ash particles at temperatures > 900°C. Therefore, no special high-temperature dust precipitation technologies are recommended.

Table 8:**Important influencing variables for efficient fractionated heavy metal separation, depending on the zone of ash precipitation for biomass fixed-bed combustion systems**

influencing variables	precipitation zone		
	grate and primary combustion zone	secondary combustion zone	boiler and downstream units
reducing atmosphere	x		
temperature of precipitation	x	x	
size of the fly ash particles		x	x
temperature range [°C]	400 - 900	800 - 1,100	< 800

At temperatures below 900°C gaseous Cd most likely forms Cd silicates or aluminosilicates by surface reactions with the fly ash particles. Zn also undergoes high-temperature surface reactions with silicates or aluminosilicates but mainly forms ZnO, most likely by adsorption of gaseous Zn to the surface of fly ash particles and subsequent oxidation as well as by homogeneous gas phase oxidation followed by condensation (the latter seems to be the most important process). The experimental results clearly revealed that these processes depend on the particle size, which means that Cd as well as Zn concentrations significantly increase with decreasing fly ash particle size (due to the larger surface area available). Submicron particles show the highest Cd and Zn concentrations. Consequently, fly ash precipitation should be particle-size selective (two-staged) and filter fly ash precipitation should be highly effective in order to minimise aerosol emissions (see Figure 14).

Fixed-bed gasification of wood chips

The results from the gasification test runs performed by DKT revealed that fluctuations of the gas flow were higher than expected and the mass balances for the individual elements did not fit as well as in the combustion experiments. Only about 60 % of the main ash-forming elements P, K, Mg and Ca were found in the ashes compared to fuel input. The rates of recovery for Cd and Zn were only 20% and 34%, respectively. The main reason for these discrepancies were probably depositions in the flue gas ducts. The bottom ash was almost free of cadmium (similar result as for the combustion test runs). The highest concentrations of Cd and Zn were found in the cyclone fly ash, precipitated immediately after the gasifier, and not in the finer fly ash particles collected further downstream. This discovery shows a behaviour of the heavy metals that is different from their behaviour in grate combustion plants where higher Cd and Zn concentrations were found in the filter fly ash compared to the cyclone fly ash. The main reason for these results seems to be the high concentration of char and tar particles which display a very porous structure and large surface area.

Utilisation of ashes from biomass gasification processes is generally difficult. Although ashes with low heavy metal concentration can be produced (bottom ash), the high concentrations of unburned carbon (and organic contaminations – mainly PAH) will increase problems concerning ash recycling on soils. Consequently, these ashes should be reburned prior to utilisation.

Technological possibilities for fractionating heavy metals within biomass combustion

CFB combustion and gasification systems

In CFBC mainly two ash streams are produced: bottom ash and filter fly ash. The results achieved in this project clearly revealed the depletion of ecologically relevant heavy metals in the bottom ash. However, due to the high amount of bed material mixed with this ash fraction, the concentrations of nutrients are also low, which renders bottom ash from CFBC unsuitable for recycling. The filter fly ash, on the other hand, contains high concentrations of K, which is an important plant nutrient lacking in Swedish forests and should be recycled. However, the results obtained during the full-scale test runs at the CFBC in Nässjö indicated that it is not possible to separate heavy metals from K in this fly ash fraction within the fluidised-bed combustion process, since both heavy metals and K react with coarse fly ash particles already at high temperatures. This fact was concluded at least at the operating conditions prevalent at the plants investigated.

However, experimental validation work carried out by UME in a bench-scale isothermal fluidised-bed reactor indicated that a somewhat higher combustion temperature (900 to 950°C) than in the investigated full-scale CFBC, should make it possible to separate Cd and Pb from the main fly ash fraction. More work is needed to determine an optimum temperature of combustion, at which most of the K could be retained in a hot cyclone fly ash fraction, while significant fractions of Cd and Pb would be separated and upgraded in a filter fly ash fraction. Here, possible sintering effects in the bed due to higher temperatures have to be considered, too.

An important question raised by VAT was whether it was necessary to separate the heavy metals from the filter ash from CFBC. Within this project, typical fly ashes from the combustion of different biomass fuels have been analysed, and the amounts of ash produced per unit of energy were also established. These facts about the ash must be related to the environmental impact, and the recycling of filter ash may be found acceptable. In Sweden, this approach seems probable - at least for ash produced by the burning of forest residues. The situation may be more problematic in the case of ash from *Salix* combustion, since the amount of Cd returned to the soil is doubled per unit of mass recycled due to the high Cd uptake of *Salix* in comparison to other wood species.

Grate combustion systems

In agreement with CFBC units, bottom ashes from grate-fired biomass combustion plants also displayed very low concentrations of heavy metals. However, as these ashes are not diluted by bed material, as is the bottom ash from CFBC, they can be used as a valuable secondary raw material with fertilising and liming effects well suitable for recycling.

Consequently the full-scale test runs in grate combustion units revealed a great potential for fractionating heavy metals within the process itself, which resulted in a number of possible technical solutions of using and enhancing this fractionation. In the following sections these ideas are described by dividing them into simple and advanced solutions for already operating combustion plants, but also guidelines for the construction of new plants.

Simple heavy metal fractionation and ash utilisation in biomass grate combustion systems

The simplest and cheapest way of using the results of fractionation obtained within the project is to inform owners and operators of district heating plants and CHP plants to separate bottom ash from fly ashes, in the case that the limiting values specified by the authorities are not met by the mixed ashes.

Bottom ash should then be distributed on agricultural fields and in forests based on a limited number of control analyses and in amounts corresponding to the actual content of nutrients needed.

The majority of existing grate-fired biomass district heating plants in Denmark and Austria have separate transport systems for bottom ash and fly ash fractions thus implying an easy possibility to collect these fractions in separate containers. The investment costs for utilising a simple heavy metal fractionation are limited to changes in the ash transport and handling system.

Advanced heavy metal fractionation systems

As has already been mentioned, state-of-the-art grate-fired combustion plants show a considerable potential for heavy metal fractionation merely by separating the different ash fractions.

However, by considering the following principles this fractionation can be further enhanced:

- By keeping the amount of bottom ash as high as possible and precipitate coarse fly ash particles in the combustion zone at high temperature. A possible way of precipitating coarse fly ash at high temperature is to utilise a hot cyclone catching large particles between the furnace and the boiler of the plant. However, results from this project and previous Austrian experiments indicate that a hot cyclone has to be operated at above 900°C in order to be efficient for heavy metal fractionation. The additional investment costs for such equipment must then be weighed against the limited amount of fly ash that can be precipitated. Moreover, the results achieved show that this approach works well only for Cd fractionation (not for Zn).

- By enlarging the grate area a lower gas velocity in the primary combustion zone can be achieved. By doing so the amount of fly ash originating from entrained particles from the grate can be reduced. This approach can be further used by introducing relaxation zones in the primary and secondary combustion zones, where coarse fly ash particles can be precipitated at high temperatures and partly also under reducing conditions.
- The fly ash separators following the boiler may be designed for particle size selective fly ash precipitation allowing for separate handling of coarse and fine fly ash particles with different heavy metal concentration levels.
- Ashes from the cyclone and final gas cleaning stage (bag house filter or ESP) should be handled separately, as the fine dust has the highest concentration level of Cd, Zn and Pb. Furthermore, fine fly ash precipitation should be efficient in order to avoid trace element emissions to the atmosphere.

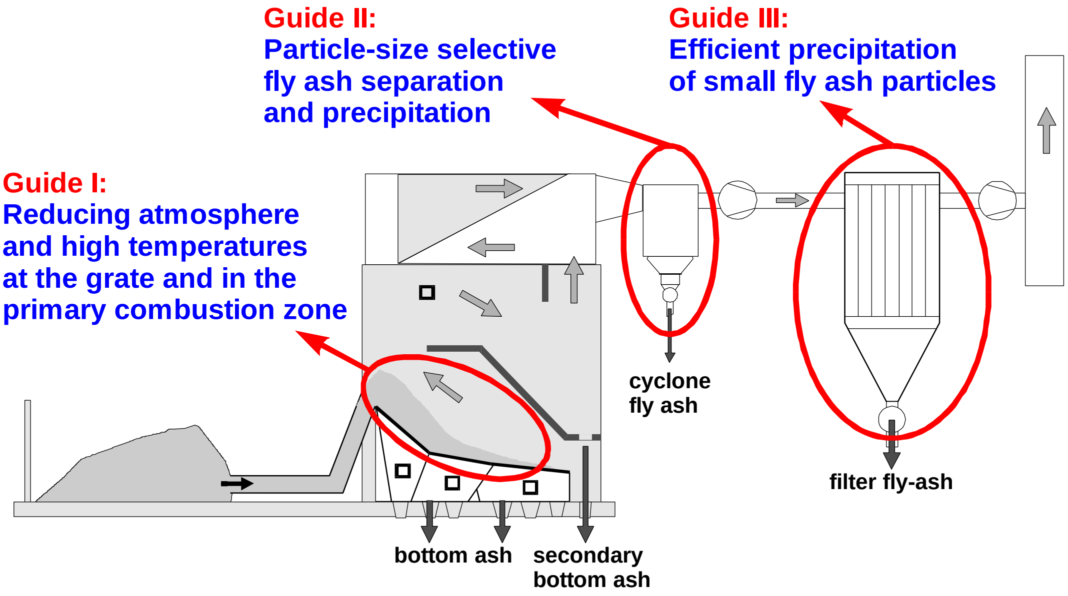
Influence and potential of appropriate process control on heavy metal fractionation

Generally the control system must ensure reducing atmosphere and high temperature on the grate and in the primary combustion zone. Mass distribution of the ash fractions as well as concentration levels of heavy metals can be influenced by an efficient air-staging technology. For optimum fractionation results, process control systems should include the following features:

- The capability to control primary and secondary air supply such that under-stoichiometric conditions are always met on the grate and in the primary combustion zone
- The capability to control primary air in a way that high amounts of bottom ash with low cadmium concentrations are kept on the grate (minimising fly ash entrainment by the flue gas).

Following the principles stated above, three general guidelines for efficient heavy metal fractionation in grate-fired biomass combustion plants can be derived (see Figure 14).

Figure 14: **Guidelines for the design of a fixed-bed combustion technology with integrated fractionated heavy metal separation**



Following the guidelines outlined, a mixture of bottom ash and coarse fly ash (particle size larger than about 5 μm) should be recycled to soils in a sustainable way. The filter fly ash (representing less than 10% of the total ash and upgraded with heavy metals) can be industrially utilised (heavy metal recovery) or otherwise has to be disposed of.

Treatment of contaminated ash fractions

From the results of CFBC, separation of heavy metals from nutrients was concluded to be difficult to perform within the process itself and, thus, a fly ash is produced that contains both heavy metals and a major part of the important nutrient K. In grate combustion units fractionation of heavy metals was concluded to be effective, but nevertheless an ash fraction is produced that has to be disposed of. Following these conclusions and the aim of closing natural mineral cycles, increased importance was attached to secondary ash treatment designed to recover plant nutrients and separate heavy metals.

Nutrient recovery and heavy metal separation by thermal treatment of contaminated biomass ashes

The behaviour of selected heavy metals in biomass filter fly ashes was studied on a laboratory scale at high temperatures in order to determine the potential of thermal treatment of contaminated ash fractions. The findings may be summarised as follows:

The efficiency of thermal ash treatment depends on the chemical composition of the glowed ash, the gaseous environment and the temperature at which glowing is performed.

Pb and Cd can be effectively separated from fly ash samples by thermal treatment at a temperature as low as 900°C in both air and N_2 provided that the ash contains at least 5 wt% combustible carbon. The separation of Zn requires higher temperatures (at least 950°C) and a more strongly reducing atmosphere before it vaporises from the ash.

Cu and As are vaporised only in minor amounts by thermal ash treatment at the conditions investigated in this study. Other research work, however, has indicated that high evaporation of Cu can be achieved by adding Cl to the ash prior to glowing [21].

Sintering of ash during thermal treatment and high concentrations of S were concluded to decrease the vaporisation of Pb and Zn. Sintering occurs in ash samples with high concentrations of K which, according to XRD analyses, are present as chloride or sulphate in biomass fly ashes. By removing KCl, K_2SO_4 and other water-soluble elements from dry precipitated ESP fly ash by leaching in water, sintering can be impeded and a higher treatment temperature can be used supporting the evaporation of heavy metals.

By addition of carbon and glowing at 950°C in N_2 the concentrations of Cd and Pb can be reduced well below the limiting values for ash utilisation in Austria (see Table 9). Under the same experimental conditions, Zn is reduced to a concentration just meeting the limiting value. Derived from trends in the results achieved, however, it is reasonable to assume that ashes with lower Zn concentrations can be produced by increased addition of carbon and higher glowing temperatures (1,000-1,100°C).

Table 9: **Concentrations of Cd in ash samples before and after thermal ash treatment in comparison to Austrian limiting values for ash utilisation**

Explanations: the resulting concentrations after glowing were achieved by glowing CS-G with 25% $C_{comb.}$ addition in N_2, glowing ESP-G with 25% $C_{comb.}$ addition in air and glowing ESP-CFB with 15wt% $C_{comb.}$ in N_2

Abbreviations: d.b....dry basis, CS-G... fluegas condensation sludge from a bark-fired grate combustion plant., ESP-G....ESP fly ash from a wood chips-fired grate combustion plant, ESP-CFB....ESP fly ash from CFBC plant in Nässjö firing forest residues

Element	Ash sample	Concentration before thermal treatment	Concentration after thermal treatment	Limiting concentrations for ash utilisation in Austria
			[mg/kg (d.b.)]	
Cd	CS-G	83	0.1	8
	ESP-G	33	0.6	8
	ESP-CFB	14	1.8	8
Pb	CS-G	610	0.5	100
	ESP-G	304	23	100
	ESP-CFB	100	38	100
Zn	CS-G	15,840	1,500	1,500
	ESP-G	3,665	1,260	1,500
	ESP-CFB	1,340	260	1,500

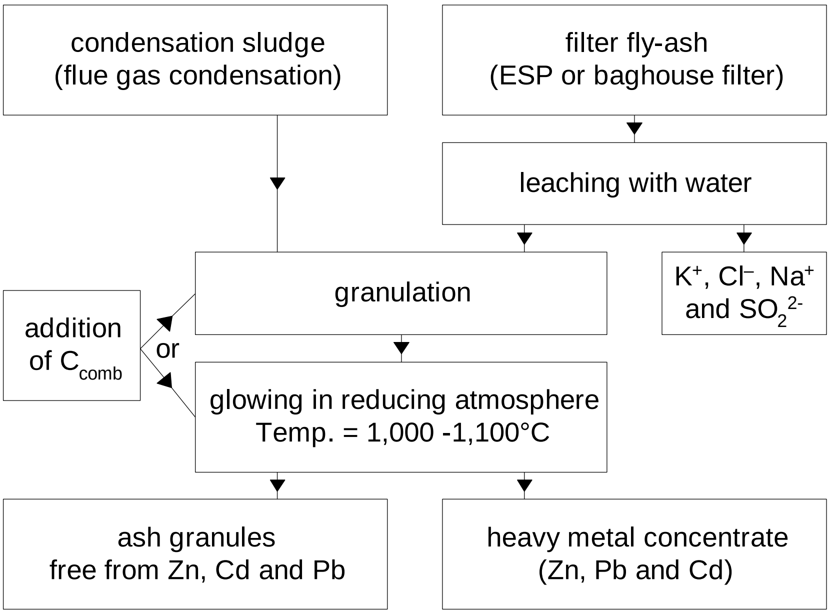
SEM micrographs of samples from layers on the cold finger revealed that they consist of submicron particles which had been formed before they precipitated on the cold surface. Chemical element analyses by EDX (energy-dispersive X-ray analyser) of dry samples and wet chemical analyses (GAAFS, ICP) of dissolved layers indicated that condensate from ESP-G fly ash consists mainly of KCl (about 90%) and condensate from CS-G ash consists mainly of metallic Zn (about 80 wt.%). The elements Na, S and Pb are found in minor amounts and Fe and P in trace amounts.

Water-soluble compounds in the condensed layers were investigated by dipping the cold finger into distilled water and then into 6% HNO_3 for a total dissolution of the layer. The results indicate that the heavy metals do not vaporise and condense as chlorides because all heavy metal chlorides are readily soluble in water (except $CuCl_2$).

The very high content of Zn, Pb and Cd and low content of Cl in the condensate from glowing CS-G ash revealed a product which is well suitable for further metallurgical processing and can be directly utilised for refined heavy metal production. By an optimised leaching step prior to glowing a similar condensate product should be achievable from ESP filter fly ashes.

Derived from the results obtained, a process consisting of two preparative steps prior to ash glowing, namely leaching in water and granulation, was developed. If condensation sludge from a flue gas condensation unit is treated, the leaching step is not necessary.

Figure 15: Steps of thermal ash treatment of contaminated fly ashes



The costs of thermal ash treatment are difficult to predict at the moment as industrial applications are not yet fully developed. However, in order to be able to be competitive, the cost of thermal ash treatment must be comparable or lower than the cost of ash disposal.

In Austria, ash disposal costs presently vary between 1,500 to 5,000 ATS per ton, depending on the concentration of pollutants in the ash.

The method of thermal ash treatment investigated in this work has been focusing on filter fly ashes from combustion of non-treated biomass. However, other ashes with the same type of contamination (Pb, Zn and Cd) could be treated with the same process.

Heavy metal recovery from contaminated ashes by bioleaching and biosorption

Leaching by inorganic acids represents a conceivable process to recover heavy metals from contaminated biomass ashes. Leaching of heavy metals (except Pb due its low solubility) by commercial organic and inorganic acids has been successful. Up to 100% of the most significant heavy metals have been extracted, thus indicating that the heavy metals are bound to the surface. The highest solubilisation rates achieved by commercial organic acids was 86% of Cr, 77% Cu, 82% Co, 100% Zn, 100% Cd, 89% Ni and 52% Pb, using 0.75N lactic acid at a pH of 3.7 (electrostatic precipitator fly ash). The respective values obtained for condensation sludge, using 0.50N lactic acid at a pH of 4.2, were Cd 100%, Cr 70%, Cu 74%, Co 77%, Zn 100%, Ni 80% and Pb 27%. As regards the mechanisms of leaching with citric, oxalic or lactic acid, heavy metals were mainly leached by acidification, because decreasing extraction of heavy metals with increasing pH was observed for all elements investigated. The extraction of Cd (up to 48%) with citric acid was rather low, Mo was leached significantly better by complex-forming agents (organic acids).

With concentrations higher than 1.0 g/L electrostatic precipitator fly ash and 2.4 g/L condensation sludge, respectively, the yield of heavy metal solubilisation by bioleaching decreased. Two-step leaching showed the highest metal yields with 1.0 g/L or 2.4 g/L of filter dust or condensation sludge, respectively. 100% of cadmium, chromium and zinc, 43 % of lead (electrostatic precipitator fly ash) and 100% of Cd, 98% of Zn, 64% of Cr, 55% of Cu, and 37% of Pb (condensation sludge) were solubilised using the acids mixture produced by *P. simplicissimum* in the two-step process. Compared to the two-step process, the leaching efficiency in the one-step process was significantly lower for zinc, chromium, cadmium and copper. The fungus *Penicillium simplicissimum* did not show high degrees of adaptation and acid production. Bioleaching cannot compare with chemical leaching - even if the C source is a cheap waste material like melasses - due to the low bioleaching capacity at increasing ash concentrations and the treatment of large volumes of contaminated effluents with relatively low metal concentrations. The aim of removing As, Cr, Cd, Cu, Mo, Ni, V and Zn from both ashes was achieved using chemical leaching with organic or inorganic acids. Since a similar concentration of extracted heavy metals is obtained with sulphuric acid, HCl or HNO_3 at pH 1.3-1.5, the use of inorganic acids is more economic because of the high price of organic acids.

The analyses showed that chemical or biological leaching could not reduce the Pb content in both ashes to such an extent that they can be spread on forest soils or agricultural fields in compliance with statutory guidelines.

The use of chemical leaching would need further ash treatment to remove Pb. Preliminary thermal ash treatment to evaporate Pb with subsequent chemical leaching could be a promising method of heavy metal removal from biomass ashes. Leaching of lead was not effective because of the low solubility of Pb compounds in aqueous solutions due to the high levels of sulphate present.

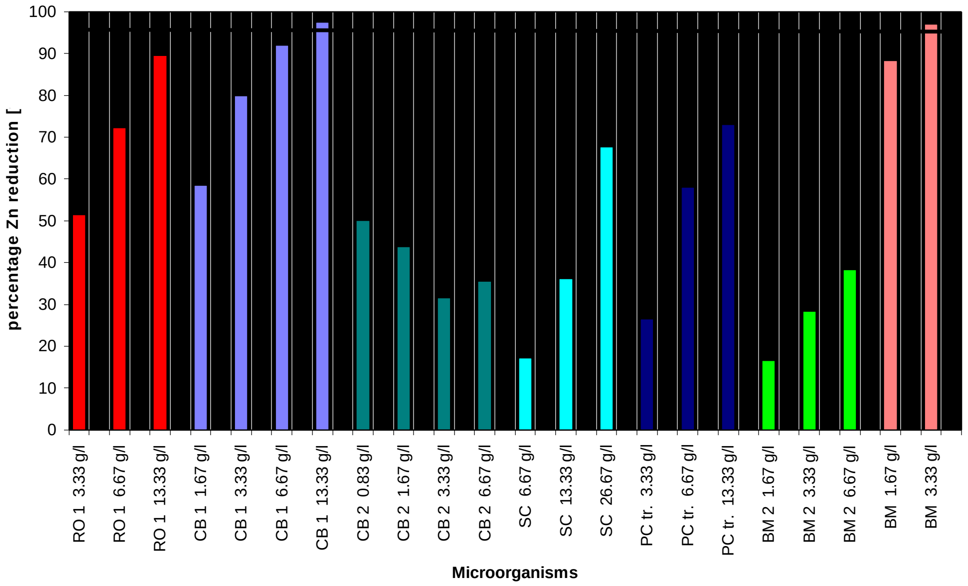
Precipitation removed 80 % of Cd, 95 % of Zn and 36 % of Ni from the leaching solution but still did not achieve the limiting values for waste water of AEVO [34].

The potential of non-living microbial biomass residues as biosorbents for heavy metals has received considerable attention, since this material represents a significant by-product from several major industrial fermentation processes. In this work it has been proved that some - but not all – waste biomass can successfully be used for heavy metal biosorption. It should also be stressed that heavy metal removal was very effective from leaching samples after precipitation indicating almost an absence of interference caused by other ions s.a. alkali metal ions. The degree of specifity of the biosorbent for the divalent and multivalent heavy metal cations is therefore an attractive feature of biosorption.

The biomass of *Cunninghamella blakesleeana* (CB), *Rhizopus oryzae* (RO) and *Bacillus megaterium* (BM) bound considerable amounts of copper and zinc from dilute single-element solutions by a non-metabolic process. Both fungi and the bacterium were able to remove 96 % (CB), 89 % (RO) and 98 % (BM) from a solution containing 50 ppm zinc at a biomass concentration of 1.6 g/L. Treatment of the fungus *Rhizopus oryzae* with NaOH greatly improved the biosorption capacity. For Cu a similar tendency was found, although the biosorbent was less effective for that heavy metal. The effect of the influence of pH on the metal accumulation of the biomass became immediately apparent. A significant reduction in the zinc biosorption capacity at a pH of 2 was observed. Heavy metal removal from single-element solutions was more effective than in the case of the simultaneous presence of metals in the waste water. This behaviour can be explained by a competition among the different metals for the same amount of adsorbent material. The kinetic data on heavy metal biosorption of the mixed metal solution (leaching solution after prec.) by *Cunninghamella blakesleeana*, determined in the course of this work, clearly indicated that the equilibrium plateau was established within 5 minutes. Cd, Zn and Ni were rapidly removed simultaneously. The processes involved – chemical complexation and adsorption – are both rapid processes. The concentration of biomass in the experiments was up to 13 g/L dry weight. The biomass of *Cunninghamella blakesleeana* and *Bacillus megaterium* KM was capable of zinc, nickel and cadmium uptake with some kind of specifity and therefore turned out to be suitable for practical use as a biosorbent for heavy metals from waste water streams, such as the leaching solutions obtained after precipitation of the bulk of the metals. Heavy metal cations such as cadmium, copper, lead and zinc were removed preferentially to the alkaline earth metals calcium, potassium and sodium.

Figure 16:: Percentage of Zn reduction (%) of leaching solutions of CS (after precipitation) by different biosorbents in comparison with the aim calculated according to Austrian limiting values for waste water (black line)

Abbr: CS..condensation sludge; BM..Bacillus megaterium KM, , CB..Cunninghamella blakesleeana, PC..Penicillium chrysogenum, PS..Penicillium simplicissimum, RO..Rhizopus oryzae, SC..Saccharomyces cerevisiae, TR..Trichothecium roseum; tr..NaOH-treated. Expl.: g/l..amount biosorbent/volume leaching solution obtained after chemical leaching and precipitation, . numbers of biosorbents stand for different cultivation media.



The best biosorbents for zinc were *Cunninghamella blakesleeana* and *Bacillus megaterium*, removing 98 % and 97 % of the total Zn content of the waste water solution at a biomass concentration of 13.3 g/L and 3.33 g/L, respectively. These heavy metal concentrations are below the Austrian limiting values for heavy metal ions in effluents (Figure 16).

The yeast species *Saccharomyces cerevisiae*, the fungal biomass of *Cunninghamella blakesleeana* and *Rhizopus oryzae* and the bacterium *Bacillus megaterium* also had the ability to remove the toxic heavy metal cadmium from the leaching solutions after precipitation (up to 94 % of Cd removed by 13.3 g/L CB, 87 % by 13.3 g/L RO and 76 % by 3.3 g/L BM), achieving the permitted values for Cd ions in waste water. A complete recovery of heavy metals was achieved. From an economic point of view, the whole process (chemical leaching, precipitation and biosorption) proved not to be economic, since the overall costs (disposal of waste products and costs of chemicals required) were higher than the costs saved on ash disposal. An economic process evaluation resulted in the conclusion that biosorption seems to be of interest only as a polishing technology in waste water treatment applications.

Exploitation and Anticipated Benefits

International research results indicate that biomass ashes contain considerable amounts of plant nutrients (P, K, Mg, Na), which makes their application on soils economically interesting for farmers. Furthermore, wood and bark ashes contain significant amounts of Ca, thus rendering them also interesting as a soil-improving agent increasing the pH level of soils. The only nutrient missing in biomass ashes is N, which is evaporated during the combustion process and thus escapes with the flue gas. The fertilizing and liming value of biomass ashes is estimated to vary between 60 and 120 ECU per ton of dry ash [35]. Consequently, biomass ashes have to be considered as valuable secondary raw materials if the heavy metal concentrations can be kept low.

Willow plantations are known to extract such amounts of cadmium that the removal of fuel crop is capable of reversing the net flow of cadmium, thus resulting in a cleansing effect. The technology under development in this project permits that the removed cadmium can be confined to a small fraction of the ash for disposal or potential recovery. However, it is not known what impact the internal metabolism of cadmium in the willow plant itself will have on the cadmium content in wheat growing on that site in the future. Given the present knowledge, the possibility of willow extracting cadmium from deeper layers of the soil and relocating it in a form available to plant by litter fall to the top cannot be excluded. The internal metabolism of cadmium and its effect on cadmium uptake in future grain crops is being researched in a project partly funded by VAT. Results are expected in approximately 2 years. As soon as this uncertainty of the real environmental advantage has been clarified the commercialisation of soil remediation in the form of *Salix* plantations, combined with fractionated heavy metal separation during thermal conversion of the *Salix* produced, will be considered.

For this reason TUG is partner in an EU Environment and Climate project which started in March 1998 and deals with the possibilities of bioremediation and economic renewal of industrially degraded land by biomass fuel crops (PL 970973), considering the possibility of fractionated heavy metal separation during thermal conversion of the crops produced. In parallel to this project TUG will, together with an Austrian boiler manufacturer, further develop the combustion technology with integrated fractionated heavy metal separation. Special focus will be placed on precipitating the total amount of usable ash on the grate by recycling the coarse fly ash collected in the multi-cyclone to the primary combustion chamber. This method is expected to result in a re-volatilisation of the major amount of Cd and Zn in the coarse fly ash particles, thus leading to a further enrichment of heavy metals in the filter fly ash. Patent applications for this technique are underway and licenses for utilising this know-how are planned to be available for all EC countries.

With the aim of making full use of the experiences gained within the project, the following activities are planned by DKT for the coming years in Denmark:

- Plant owners and operators will be informed about the possibilities of ash recycling and the fractionation of heavy metals (simple as well as advanced) in grate-fired combustion systems
- Tests and development projects concerning the method of efficient fractionated heavy metal separation in grate-fired systems developed and recommended by TUG will be initiated.
- Experience concerning the correct analysis of biomass fuels and ashes gained from the work in this project will be used in future projects.

The cadmium situation in relation to the developed technology and its market value is another important aspect for the exploitation of the results achieved in the project. Most likely, commercialisation on a European scale will not take place until such an analysis is available. Thus, VAT and TUG are partners in a Thermie B project (“The market implications of integrated management of heavy metal flows for bioenergy use in the EU”) covering these aspects. The project proposed includes the application of similar chains of growing specific metal-extracting plants on heavily contaminated industrial sites as well as technologies for fractionation and recovery of the metals in a form suitable for safe disposal or recovery. In connection with this project, applied research on strategic and economic aspects of thermal ash treatment based on the results of this project will be performed before pilot-scale experiments should be carried out together with an industrial partner. This work is planned for the years 1999 to 2001, and after that the possibility of a wider and more general commercialisation will be evaluated.

Furthermore, the results from particle formation, aerosol modelling and heavy metal behaviour may be utilised by the manufacturers of fluidised-bed boilers to minimise the ash-related risks from the boilers and to make a re-circulation of the ash possible. Also, the users of the boilers, e.g. power plant utilities, waste incinerators as well as pulp and paper mills may use the results to optimise the operation of the existing boilers with regard to ash-related issues.
The results of this project will be adapted by VTT for such R&D activities with major boiler manufacturers and utility companies in Finland.

The emission control of ultrafine particles formed in combustion processes has become an important issue due to recent findings of adverse health effects of ambient fine particles. The understanding of ash formation is vital for the development of fine ash control methods, such as advanced electrostatic precipitators and fabric filters. The results of this study will be utilised by VTT and its industrial partners in such an effort.

The conceptual aerosol model that was developed in this work may be used to describe the behaviour of the volatilised species in other combustion processes. This will lead to a better understanding of the ash formation and transformations during combustion and gasification. If necessary, the agglomerate model may also be incorporated into existing models describing ash transformations to develop advanced models for new combustion processes, an effort being carried out at VTT Aerosol Technology Group.

Chemical equilibrium model calculations used in this project will be further developed by UME by continuously updating the thermodynamic database used in the model. New fundamental thermochemical data on the complex chemistry of heavy metals will be achieved by sorbent experiments as well as kinetic studies. An improved model will be helpful for understanding and explaining the behaviour of heavy metals during combustion and gasification processes. The promising results from the isothermal bench-scale BFB reactor constructed within the project will be used for further investigations on in-situ separation of heavy metals from nutrients (especially K) at relatively high temperatures.

Finally, the process comprising chemical leaching, precipitation and biosorption proved to be not economic. However, the biosorption step alone seems to be of interest as a polishing technology in waste water treatment applications, offering a potential alternative and a supplement to existing methods of heavy metal removal.
There is a potential for the development of a process to remove or recover heavy metals from waste water using the kind of biomass investigated by TUG within this project. It should be stressed that technologies based on biosorption should not necessarily replace existing waste water treatments but may complement them in optimised processes. At present, some conventional techniques (e.g. precipitation) are at their limits as regards the removal of heavy metals from effluents. Biosorption systems in combination with existing processes offer an interesting possibility for achieving the strict limiting values for waste water.

REFERENCES

1 OBERNBERGER, J. DAHL, A. ARICH (1998): Biomass fuel and ash analysis, report of the European Commission DG XII (ed.), Brussels, Belgium, ISBN 92-828-3257-0

2 OBERNBERGER Ingwald, BIEDERMANN Friedrich (1998): Fractionated heavy metal separation in Austrian grate fired biomass combustion plants – approach, experiences, results, In: Ashes and particulate emissions from biomass combustion, Series Thermal Biomass Utilization, Volume 3, BIOS (ed.), Graz, Austria, dbv-Verlag, ISBN- 3-7041-0254-7

3 NORDIN, Anders (1993): On the chemistry of combustion and gasification of biomass fuels; Environmental aspects. Thesis (PhD), Umeå University, Sweden

4 NORDIN Anders (1994): Chemical elemental characteristics of biomass fuels. Biomass and Bioenergy, 1994, 6, 339-34

5 BOX G. E. P., HUNTER W. G., HUNTER J. S. (1978): Statistics for experimenters; An introduction to design, data analysis and model building. Wiley, New York, USA

6 UMETRI AB (1995): MODDE "Modelling and design, users guide", (1995), Vol 3.0, Umetri AB, Umeå, Sweden

7 KAUPPINEN E.I. (1992): On the determination of continuos submicron liquid aerosol size distributions with low pressure impactors, Aerosol Sci. Technol., 16, pp.171-197.

8 KAUPPINEN, E., PAKKANEN, T. (1990): Coal combustion aerosols: a field study, Environ. Sci. Technol. 24 pp. 1811 - 1818

9 BUNDESMINISTERIUM FÜR LAND- UND FORSTWIRTSCHAFT (1997): Der sachgerechte Einsatz von Pflanzenaschen im Acker- und Grünland, guideline (2nd draft), Federal Ministry for Agriculture and Forestry (ed), Vienna, Austria

10 BUNDESMINISTERIUM FÜR LAND- UND FORSTWIRTSCHAFT (1997): Der sachgerechte Einsatz von Pflanzenaschen im Wald, guideline, Federal Ministry for Agriculture and Forestry (ed), Vienna, Austria

11 BURGSTALLER W., STRASSER H., WÖBKING H., SCHINNER F. (1992): Solubilization of Zinc Oxide from Filter Dust with Penicillium simplicissimum. Bioreactor Leaching and Stoichiometry. Environ. Sci. Technol., 26/2, 340-46.

12 VOLESKY B. (1987): Biosorbents for Metal Recovery. TIBTECH, 5/4, 96-101.

13 HORIKOSHI T., NAKAJIMA A., SAKAGUCHI T. (1981): Studies on the Accumulation of Heavy Metal Elements in Biological Systems. Eur. J. Appl. Microbiol. Biotechnol., 12, 90-96.

14 NAKAJIMA A., SAKAGUCHI T. (1986): Selective Accumulation of Heavy Metals by Microorganisms. Appl. Microbiol. Biotechnol., 24, 59-64

15 MARQUIS R.E., MAYZEL K., CARTENSEN E.L. (1976): Cation Exchange in Cell Walls of Gram-positive Bacteria. Can. J. Microbiol. 22, 975-982.

16 NORRIS P.R., KELLY D.P. (1979): Accumulation of Metals by Bacteria and Yeasts. Dev. Ind. Microbiol., 20, 299-308.

17 HU M. Z.-C., NORMAN J.M., FAISON B.D., REEVES M.E. (1996): Biosorption of Uranium by Ps. aeruginosa Strain CSU. Charakterisation and Comparison Studies. Biotechn. and Bioengin. 51, 237-247

18 KLEPPE M., LIETZ W. (1992): Biosorption of Heavy Metals from Leachates. In: Soil Decontamination Using Biological Processes, Preprints, International Symposium Karlsruhe, 6-9 Dezember 1992, Dechema (ed), Deutsche Gesellschaft für Chemisches Apparatewesen, Chemische Technik und Biotechnologie, Germany

19 LUEF E., PREY T., KUBICEK C.P. (1991): Biosorption of Zinc by Fungal Mycelial Wastes. Appl. Microbiol. Biotechnol., 43, 688-92.

20 VOLESKY B. (1990): Removal and Recovery of Heavy Metals by Biosorption. in: Volesky B.(ed.): Biosorption of Heavy Metals. pp 8-43, CRC PRess, Boca Raton.

21 JAKOB Aldo, STUCKI Samuel and KUHN P. (1995): Evaporation of Heavy Metals during the Heat Treatment of Municipal Solid Waste Incineration Fly Ash, Environ. Sci Technol. 1995, Vol 29, pp 2429-2436

22 JACOB Aldo, STUCKI Samuel, STRUIS R. P. W. J. (1996): Environ. Sci. Technol. 30, 3275-3283

23 HINDS, W.C. (1982): Aerosol Technology. Properties, behaviour, and measurement of airborne particles. John Wiley & Sons, New York

24 SCHLEICHER B., KUNZEL S. and BURTSCHER H. (1995) J. Appl. Phys., 78, pp. 4416-4422.

25 LIND T., KAUPPINEN E. I., SFIRIS G., NILSSON K. and MAENHAUT W. (1997) Fly Ash Deposition onto the Convective Heat Exchangers during Combustion of Willow in a Circulating Fluidized Bed Boiler. Accepted for publication in 'The Impact of Mineral Impurities in Solid Fuel Combustion'. Proceedings of the Engineering Foundation Conference, Kona, HI, November 2-7, 1997, 14 p

26 VALMARI T., LIND T., KAUPPINEN E. I., SFIRIS G., NILSSON K. and MAENHAUT W. (1998a): Ash Transformations during Circulating Fluidized Bed Combustion of Forest residues and Willow: 1. Ash Formation. Submitted to Energy&Fuel

27 VALMARI T., LIND T., KAUPPINEN E. I., SFIRIS G., NILSSON K. and MAENHAUT W. (1998b): Ash Transformations during Circulating Fluidized Bed Combustion of Forest residues and Willow: 2. Ash Deposition and Fine Particle Formation. Submitted to Energy&Fuels.

28 LIND T., VALMARI T., KAUPPINEN E. I., SFIRIS G., NILSSON K. and MAENHAUT W. (1998a): Volatilization of the Heavy Metals during Circulating Fluidized Bed Combustion of Forest residues. Submitted to Environ. Sci. Techn.

29 LIND T., KAUPPINEN E.I., NILSSON K., SFIRIS G., MAENHAUT W. and HUGGINS F.E. (1998b): Heavy metal behaviour during circulating fluidized bed combustion of willow (*Salix*). Accepted for presentation at 15th International Conf. on Fluidized Bed Combustion, May 9-13, 1999, Savannah, Georgia, USA.

30 ERIKSSON J. (1993): Karakterisering av vedaska (in Swedish). Rapport från Vattenfall Research Bioenergi, UB 1993/48, ISSN 1100-5130

31 CRC (1997): CRC Handbook of chemistry and physics, 78th edition 1997-1998. CRC Press, Boca Raton, Florida, USA

32 LJUNG Anders, NORDIN Anders (1997): Theoretical Feasibility for Ecological Biomass Ash Recirculation; Chemical Equilibrium Behaviour of Nutrient Elements and Heavy Metals During Combustion, Environ. Sci. Technol., 1997, 31, 2499-2503

33 CHRISTENSEN K.A. (1995): The formation of submicron particles from the combustion of straw, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark

34 AUSTRIAN FEDERAL MINESTRY OF ENVIRONMENT (1991): AEVO: Allgemeine Österreichische Abwasseremissionsverordnung (Austrian limiting values for waste water disposal into rivers or sewers), BGBl. 18179 (1991)

35 RUCKENBAUER Peter, OBERNBERGER Ingwald, HOLZNER Heinrich (1996): Erfor-schung der Verwendungs-möglich-keiten von Aschen aus Hackgut- und Rindenfeue-rungen, final report, part II of the research project No StU 48 - Bund-Bundesländerkoope-ration, Institute of Plant Breeding and Plant Growing (ed), University for Agriculture and Forestry, Vienna, Austria