

THERMODYNAMIC AND EXPERIMENTAL INVESTIGATIONS ON THE POSSIBILITIES OF HEAVY METAL RECOVERY FROM CONTAMINATED BIOMASS ASHES BY THERMAL TREATMENT

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ABSTRACT: In the framework of the EC-JOULE project "Sustainable Ash Utilization" research is focused on the possibilities of heavy metal recovery from contaminated filter fly-ashes in order to be able to recycle the decontaminated ashes on soils and use the metals in industrial processing. Thermal ash treatment under controlled conditions was applied to achieve this objective. Glowing contaminated ashes under controlled conditions as regards temperature and gas atmosphere offers the possibility to vaporise the ecologically relevant heavy metals (Cd, Zn) and subsequently separate their condensed species by appropriate measures. Two approaches are followed in this investigation: laboratory glowing experiments on three different types of fly ashes in different gas atmospheres and at different temperatures with subsequent calculation of phase and reaction equilibria on the basis of minimising Gibbs free energy, using the HSC computer program, and comparison of the calculated results with the results obtained from the experiments. The main emphasis of this investigation is placed on identifying influencing parameters and explaining them with the help of the theoretical calculations. The results of these studies will help to establish a theory on the behaviour of heavy metals and other important ash elements (like K, S, Cl) in high-temperature atmospheres. Finally, the results will help in developing and evaluating a technology for separating and recovering heavy metals from contaminated fly ashes. The highest percentages of heavy metal reduction by thermal ash treatment are achieved in a reducing atmosphere, which is created or enhanced by organic carbon in the ashes. It could be proved that the aims of separation according to the Austrian regulations for ash utilisation can be reached by this method. Ash samples rich in Si and ash samples which sinter during the thermal treatment negatively affect the evaporation of heavy metals. The present state of modelling the heavy metal behaviour with chemical equilibrium calculations is not consistent with the results achieved for Zn in the experiments, but gives possible explanations for the behaviour of Cd.

1 INTRODUCTION AND BACKGROUND

Three types of ashes are produced in a biomass district heating plant: bottom ash, cyclone fly-ash and filter fly-ash. If the plant is equipped with a flue gas condensation unit, the filter fly-ash will be precipitated as condensation sludge, otherwise as ESP ash or fibrous filter ash. As ashes produced from biomass combustion contain considerable amounts of important plant nutrients a recycling to forests and agricultural fields is an important factor for the sustainability of thermal biomass utilisation. However, due to dry and wet depositions in forests, environmentally harmful heavy metals (primarily Cd and secondly Zn) are introduced into the combustion plant with the biomass fuel and finally end up in the ash. As a result of the fractionation of these volatile heavy metals (Cd and Zn) within the combustion process the major amounts of these metals are found in the filter fly ash fraction.

In January 1997 Austrian guidelines [1] on maximum heavy metal concentrations for the application of biomass ashes on forest soils entered into force. The limiting values for Cd and Zn are shown as values A in Table 1. By comparing these limiting values with the average concentration of Cd and Zn found in woody biomass ash fractions, calculated from 6 Austrian biomass combustion plants using different kinds of biomass fuels (bark, wood chips, sawdust), it can be seen that a mixture of bottom ash and cyclone fly ash will fulfil these regulations, but

the filter fly-ash exceeds the concentration limits for the heavy metals Cd and Zn significantly

However, aiming at future sustainable biomass utilisation, the limiting values will decrease towards the allowed concentrations in the soil itself [2]. These values (B in Table 1) are considerably lower than the present limiting values (A in Table 1).

Table 1: The average concentrations [mg/kg (d.b.)] of Cd and Zn in average Austrian biomass ash fractions compared to limiting values

Abbreviations: AAustrian limiting values for ash utilisation [1]
 B.....guiding values for Austrian soils [2]
 MV.....mean value
 STD.....standard deviation

	bottom ash		cyclone fly-ash		filter fly-ash		A	B
	MV	STD	MV	STD	MV	STD		
Cd	1.2	0.7	21.6	8.1	80.7	59.2	8	1
Zn	433	306	1,871	599	12,981	12,196	1,500	300

From Table 1 it is also obvious that by applying the strict guiding values for soil concentrations even the mixture of bottom ash and cyclone fly-ash will require a reduction in Cd and Zn in the future. Ongoing Austrian R&D projects [3] have shown promising results concerning the possibility and potential of fractionated heavy metal separation in new biomass combustion plants. This new technology reduces the concentrations in the bottom ash

and the cyclone fly-ash, while upgrading the heavy metals in the filter fly-ash. Filter fly-ash treatment is therefore expected to be of growing importance.

2 OBJECTIVES

The present project aims at investigating parameters that influence the vaporization of heavy metals from contaminated biomass ashes in order to reveal the potential of thermal treatment for the decontamination of ashes from biomass district heating plants. The investigation is primarily focused on the ecologically most relevant heavy metals in biomass ashes (Cd and Zn).

The scope of work includes the development of a process for removing these elements from highly contaminated ashes in order to obtain a non-toxic ash fraction that can be returned to forest soils or agricultural fields. The reduction goals are therefore set according to the corresponding Austrian guidelines for ash utilisation outlined in Table 1. Furthermore, the heavy metals separated should be recovered and industrially utilised.

3 METHODOLOGY

Fly ashes from three different biomass district heating plants were glowing in a laboratory-scale equipment at different temperatures (900, 950 and 1000°C) and in controlled gaseous atmospheres. Two gases were used, N₂ and air, creating a reducing or an oxidising atmosphere, respectively. Each experiment continued for 1 hour and the gas flow was 0.002 Nm³/h. The toxic heavy metals Zn and Cd are separated from the ash sample by evaporation and subsequently collected by condensation on a cold surface that is introduced into the hot gas flow (see Figure 1). Particles and gases that do not precipitate on the cold surface are caught in a gas-washing bottle filled with 6 % HNO₃ acid and connected to the outlet from the oven of the purge gas.

The layers condensed on the cold surface were dissolved in 6 % HNO₃ acid and the solutions were analysed by atomic adsorption spectrometry (FAAS). Furthermore, the ash samples were analysed before and after the respective glowing experiments, and the solutions in the gas washing bottle were also subjected to detailed analyses.

Moreover, high temperature equilibrium calculations simulating the conditions of the glowing experiments were performed and evaluated in order to understand the chemical reactions and behaviour of the heavy metals investigated.

3.1 Ashes used in the glowing experiments

Three filter fly-ashes from different biomass combustion plants were investigated. The ashes were chosen as they are highly contaminated with heavy metals but differ in their chemical composition. The samples included a fly ash collected by an electrostatic precipitator (ESP) from a grate combustion plant burning wood chips, a dried condensation sludge (CS) from a grate furnace burning bark, and another ESP fly ash from a circulating fluidized bed (CFB) combustion plant burning forest residues. The average concentrations of important elements in the different ashes are displayed in Table II. The condensation

sludge contains the highest concentrations of heavy metals due to the fact that the main part of the water soluble elements (K, Cl and S) has been removed by dissolution in the condensate water. The ESP filter fly ash from the CFB unit contains high amounts of Si from the bed material in the CFB which dilutes the fly ash and thus lowers the heavy metal content.

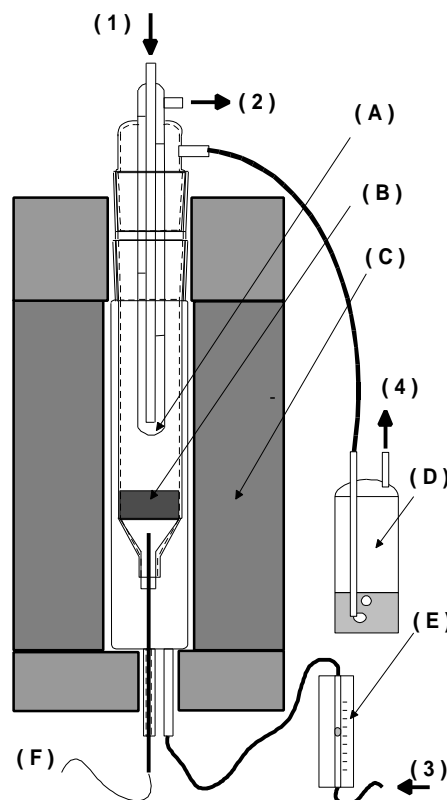


Figure 1: Outline of experimental set-up

- Explanations:
- (1) inlet of cooling water, T=50°C
 - (2) outlet of cooling water
 - (3) inlet of purge gas (air or N₂)
 - (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 II: Overview of the average concentrations [mg/kg ash (dry basis)] of important elements in the ashes investigated

Abbreviations: ESP.....ESP filter fly ash
 CS.....condensation sludge
 CFB.... ESP filter fly ash from a CFB combustion unit
 C_{org}.....organic carbon

element	ESP	CS	CFB
	mg/kg (d.b.)		
Cd	33	83	14
Zn	3,665	15,547	1,340
K	92,498	6,753	45,600
S	44,824	12,374	22,000
Cl	9,480	265	14,800
Si	11,208	22,825	136,000
C_{org}	68,600	50,400	12,000

4 RESULTS

About 80 to 95 % of the vaporised species were found on the cold finger after the experiments. 0.5-1.5% were found in the gas washing bottle. The rest was not found due to incomplete sampling or inaccuracy in the analyses.

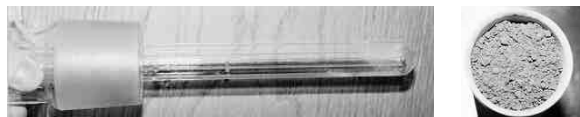


Figure 2: Cold finger and ash sample before glowing experiment



Figure 3: Cold finger with precipitate and ash sample after glowing ESP filter fly ash



Figure 4: Cold finger with precipitate and ash sample after glowing condensation sludge in N₂

Analyses of the precipitate on the cold finger by raster electron microscopy (EDAX) as well as FAAS analyses of the precipitate dissolved in acid showed that the main part of the evaporated and precipitated elements are K, Na, Cl, and Zn. S is also a main element in layers collected from experiments performed with air as purge gas. Sulphation of precipitated chloride compounds is the most likely explanation for this effect. Moreover, small amounts Pb, P and Fe were also found in the precipitate.

O₂ was identified by the raster electron microscopy analyses but could not be correctly quantified due to oxidation of the sample surface. In the acid solutions O₂ could not be analysed. Therefore, a quantification of O₂ could not be performed. On the basis of the other elements analyzed, however, it was estimated that the white precipitate from the experiments with ESP filter fly-ash consists of about 80-85% KCl and 5-10% NaCl and the black precipitate on the cold finger in the condensation sludge experiments with N₂ as purge gas consists of about 85% Zn. ZnO is white and can thus be excluded as a possible compound.

The ESP filter fly ash sintered during the glowing experiments (Figure 3) at all temperatures investigated, whereas CS (Figure 4) and CFB ashes did not display any sintering behaviour.

4.1 Percentage reduction of heavy metals by thermal treatment

The most common industrial processes of Zn and Cd production involve the reduction of ZnO and CdO to Zn and Cd, respectively. Separation is achieved by heating ores together with coke at high temperatures (1100°C), resulting in evaporation. Considering this process and the low concentrations in biomass bottom ashes the influence of adding carbon to the ash samples was investigated as well. For the glowing experiments in air an amount of carbon corresponding to 25 wt% of the sample was added

to each sample. For the glowing experiments in N₂ different amounts of carbon were added such that each sample contained 15 wt% unburned carbon after addition. (CS+C see Figure 5).

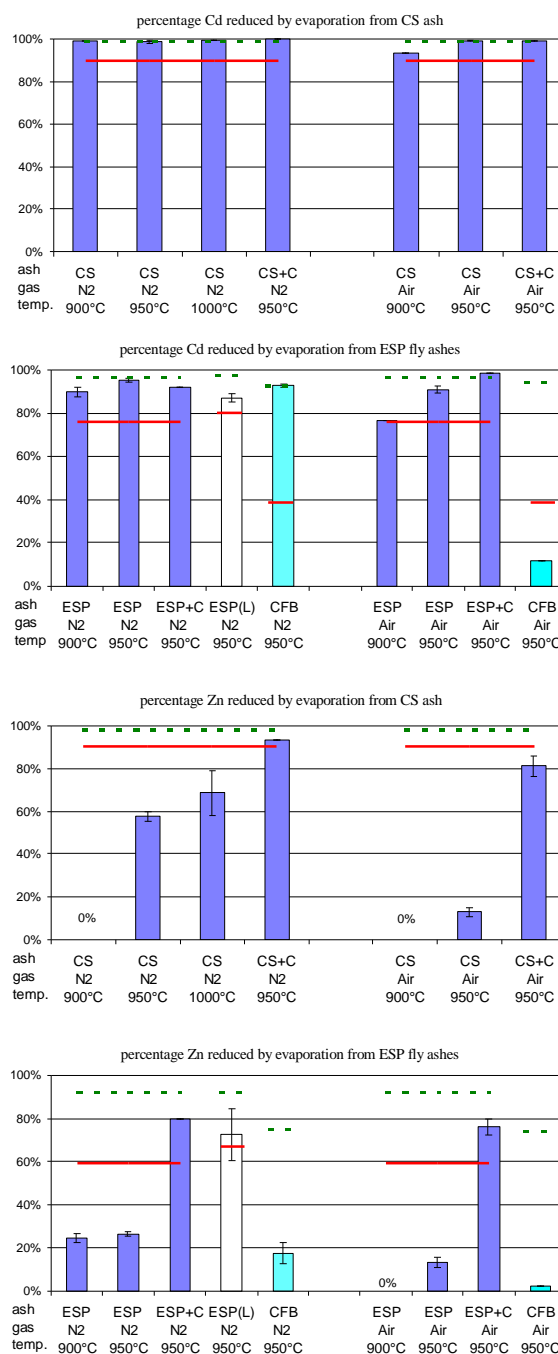


Figure 5 : Percentage of Cd and Zn reduction obtained in comparison with aims calculated according to Austrian limiting values for ash utilisation in forests and on agricultural fields (black lines) as well as the allowed concentration in soils (grey dashed lines)

Abbreviations: CS+C.....condensation sludge with carbon addition
 ESP+C.....ESP filter fly ash with carbon addition
 ESP(L).....ESP filter fly ash leached in water
 CFB.....ESP filter fly ash from a CFB combustion unit

Explanations: Due to the fact that the concentrations of heavy metals are different in the ESP, ESP(L) and the CFB fly ashes the aims of heavy metal reduction are different, as well.

Moreover, in order to investigate the effect on the evaporation of heavy metals due to the lack of water soluble elements (K, Na, Cl and S) in the CS ash, ESP ash leached in water prior to the glowing experiments were investigated, as well (ESP (L) in Figure 5)

4.2 Thermodynamic equilibrium calculations

High-temperature multicomponent and multiphase chemical equilibrium calculations were performed using the HSC program [4]. Input data were taken from the experiments performed with the three different fly ashes. The molar amounts of the elements Al, As, C, Ca, Cd, Cl, H, Fe, K, Mg, N, Na, O, P, Pb, S, Si, and Zn in each ash sample used in the glowing experiments as well as the total amount of gas used during each experiment served as input data for the equilibrium calculations, which were performed for temperatures between 300 and 1000°C. The model is based on 76 gaseous and 58 solid compounds specified as stable compounds on the basis of previous calculations concerning biomass ashes [5]. In addition to this database, the heavy metal compounds $ZnFe_2O_3$, Zn_2SiO_4 , $ZnSiO_3$ and $CdSiO_4$ were considered in the calculations with HSC.

In the model all gaseous species were considered as ideally mixed, while all condensed species were considered as immiscible solid phases. Calculations were performed for both the experiments in reducing (N_2) and oxidizing (air) atmospheres and at the glowing temperatures investigated (900-1000°C).

The results from the chemical equilibrium calculations, showed interesting differences in the behaviour of Cd between the results obtained for the CFB ash and the other two ashes. The CFB ash contains a much higher amount of Si. In the calculations for the CFB ash, $CdSiO_4$ was found to be stable up to 1000°C in oxidizing atmospheres, but evaporates as Cd (g) at 550°C in reducing atmospheres. No $CdSiO_4$ was found to be stable in the calculations of the ESP and the CS ash in oxidizing atmospheres. Instead, Cd evaporates as $CdCl_2(g)$ or $Cd(g)$ at 870°C and 920°C, respectively. These results are in good agreement with the results achieved from the glowing experiments, where the CFB ash showed the lowest separation results for Cd compared to the other two ashes glowed in oxidizing atmospheres. The high volatility of Cd in the reducing atmosphere is also consistent with the results of the glowing experiments.

The results from the calculations predicted Zn to be more refractory than displayed by the experiments. The calculations suggest that Zn is stable as solid ZnO or $ZnSiO_3$ (CFB ash) in oxidizing atmospheres at high temperatures (1000°C), and as solid ZnS or Zn_2SiO_4 (CFB ash) in reducing atmospheres. On the contrary, the experimental results revealed that in reducing atmospheres major parts of Zn should be in the gaseous phase at temperatures above 950°C (see figure 5)

5 DISCUSSION AND CONCLUSIONS

The efficiency of thermal ash treatment depends on the chemical composition of the ashes, the gaseous environment and the temperature at which the treatment is performed. The addition of carbon and subsequent glowing at 950°C all ashes made it possible for all ash

samples to achieve the reduction targets of Zn and Cd calculated according to Austrian regulations for ash utilisation in forests. Cd can be effectively separated from the ash samples by thermal treatment at a temperature as low as 900°C, while the separation of Zn requires temperatures above 908°C, which is the atmosphere boiling point of Zn. $ZnCl_2$ has a atmospheric boiling temperature at 732°C, which explains the minor evaporation of Zn from the ESP ash at 900°C.

The concentration of unburned carbon in the ash samples probably has the strongest influence on the separation results, provided that the temperature used for thermal treatment is high enough. The highest percentages of separation of the heavy metals Cd and Zn were generally achieved for ash samples with carbon addition.

However, other parameters, like sintering of the ashes during treatment, also affect the results of separation. The percentage of evaporation of Zn decreases when the ash starts to sinter. The sintering process occurs in the ESP fly-ash samples, which contain high concentrations of K. By removing K and other water-soluble elements from the ESP fly-ash by leaching in water, sintering can be impeded, which results in a higher percentage of evaporation.

CFB ash samples, which have the highest Si content and lowest concentration of unburned carbon of all fly-ash samples investigated, also displayed the lowest percentage of separation of heavy metals. Chemical equilibrium calculations indicate that refractory heavy metal silicates could be formed, but cannot explain the high percentage of evaporated Zn in the other ash samples investigated. Consequently, an improvement of the model (concerning the database used for the heavy metal compounds) is necessary before the calculations can be used for explaining the behaviour of the heavy metals during thermal ash treatment.

ACKNOWLEDGMENT

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