

Studies on Ash Behavior during Co-Combustion Of Paper Sludge in Fluidized Bed Boilers

Untersuchung des Ascheverhaltens bei der
Mitverbrennung von Papierschlamm in
Wirbelschichtfeuerungen

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Preface

The present doctoral thesis has been performed in the framework of the EU research project “Reduction of Toxic Emissions from Co-Combustion of Coal, Biomass and Waste in Fluidised Bed” (EU Contract No. JOF3-CT97-0191). The main aims of the project were the widening the spectrum of fuels utilised by coal-fired, coal-straw fired, biomass-fired fluidised bed boilers, the improvement of the potential to use energy-containing residues, and the assessment of the environmental impact of waste co-firing by investigating in particular the toxic trace metals emissions. A substantial part of this thesis represents the contribution of the Institute of Process Engineering and Power Plant Technology (IVD), University of Stuttgart, Germany, to this EU project, especially as far as experimental results are concerned.

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ZUSAMMENFASSUNG

Der Schwerpunkt der vorliegenden Arbeit liegt auf der Untersuchung des Anreicherungs- und Emissionsverhaltens von toxischen Schwermetallen bei der Mitverbrennung von Papierschlamm mit Kohle und Biomasse in der Wirbelschichtverbrennungsanlage zur Strom- und Warmerzeugung.

Die vorliegende Arbeit entstand im Rahmen eines europäischen Forschungsprojekts, welches das Ziel hatte, das Spektrum möglicher Brennstoffe die in einer Kohle und Kohle/Stroh Wirbelschichtfeuerungsanlage verbrannt werden können zu erweitern. Es sollten die Umweltauswirkungen und potentielle Betriebsprobleme dieser Abfallmitverbrennung bewertet werden.

Hierfür wurde das Verhalten der verschiedenen Aschebestandteile bei der Wirbelschichtmitverbrennung bestimmt. Verschiedene Untersuchungen zeigten, dass die Interaktionen zwischen der Biomasse und den anorganischen Bestandteilen der Abfälle mit den Kohleaschebestandteilen zu Betriebsproblemen wie Verschmutzungen, Verschlackungen und Korrosion führen können. Da diese Schädigungen die Anwendung der Ersatzbrennstoffe begrenzen können, ist es sehr wichtig die potentiellen Probleme für die Wirbelschichtfeuerungsanlage, z.B. Ascheverschmutzungen auf dem Wärmetauscher und Betttagglomeration, einzuschätzen.

Untersuchungen zur Anreicherung der toxischen Spurenelemente (z.B. Cd, Cu, Pb, Zn) bei der Mitverbrennung von Papierschlamm werden dadurch begründet, dass manche Spurenelemente im Papierschlamm in sehr hohen Konzentrationen zu finden sind, welche zu erheblichen Umwelt- und Gesundheitsschäden führen können.

Der experimentelle Teil der Arbeit wurde in zwei Bereiche geteilt:

- 1) Verbrennungsuntersuchungen mit Papierschlamm als Einzel-Brennstoff: Dabei wurde das Verhalten unterschiedlicher Papierschlämme (Schlamm von primär mechanischen Trenn-Prozessen, und Deinking Schlamm) in einer Versuchs-Wirbelschichtfeuerungsanlage (30 KWth) untersucht.
- 2) Mitverbrennungsuntersuchungen: Diese Arbeit konzentrierte sich auf Untersuchungen mit Papierschlämmen als Ersatzbrennstoffe zusammen mit Kohle und Stroh als Hauptbrennstoffe (Mischungen von Kohle und Stroh 50%/50% auf Heizwertbasis). Diese Versuche wurden auch an der Versuchsanlage durchgeführt. Der Papierschlamm ersetzte dabei bis zu 25% der Hauptbrennstoffe.

Den ersten Schwerpunkt der Arbeit bildete die Untersuchung des Ascheverhaltens bei der Mitverbrennung von Kohle und Kohle/Stroh mit Papierschlamm. Die wichtigste Frage dabei war wie die unterschiedlichen Brennstoffe die Verbrennungseigenschaften und die Ascheeinbindung der toxischen Spurenelemente beeinflussen. Die Mitverbrennung mit Kohle und Stroh wurde untersucht weil ein großes Interesse bestand, das Verhalten dieser Brennstoffe bei der Mitverbrennung kennen zu lernen, da die 3 Brennstoffe zusammen in einer zirkulierenden Wirbelschichtfeuerung mit 80 MWth verbrannt werden sollten. Durch die Untersuchungen sollte das Spektrum der zu verbrennenden Brennstoffe erweitert werden, um den Anteil fossiler Brennstoffe zu reduzieren.

Die Entnahme der Aschenproben war der erste Schritt, um das Asche-Verhalten mit Hilfe von Massenbilanzen und Berechnungsanalysen zu charakterisieren. Die Massenbilanzen für eine SWS/ZWS Feuerungsanlage sind normalerweise von dem Bettmaterial beeinflusst. Flugasche und Bettasche wurden in Abhängigkeit der unterschiedlichen Brennstoffparameter untersucht.

Von speziellem Interesse war das Verhalten von Schwefel, Chlor und Alkalien, die Ascheablagerungen im Rauchgasweg bewirken können. Außerdem können erhöhte Alkalienkonzentrationen Bettagglomerationen in der Feuerungsanlage hervorrufen. Die anorganischen Elemente mit der höchsten Konzentration in der Papierschlamm-Asche sind Al und Ca, die von Papierfüllstoffen wie Kaolin und Kalkspat stammen. Die Auswirkung von Al, Si und Ca auf die Anreicherung von Chlor wurde ebenfalls untersucht. Das Verhalten von Cu, Zn, Mn, Pb, Cd bei der Verbrennung wurde ebenfalls untersucht. Diese Elemente wurden wegen ihres hohen Umwelt- und Gesundheitsschädigungspotentials gewählt. Es wurde die Aufteilung dieser Elemente zwischen Bettasche, Flugasche (eine grobe Fraktion und eine feine Fraktion) und Rauchgas untersucht.

Die experimentellen Ergebnisse wurden mit Gleichgewichtsberechnungen verglichen, die spezifisch für die ausgewählten Brennstoffe von der Åbo Akademi Combustion Research Department durchgeführt wurden. Die Rechnungen zeigen die Bildung von stabilen kondensierten und gasförmigen Komponenten in einem breiten Temperaturspektrum (400-1200°C). Für die Gleichgewichtsberechnung wurde das Programm FACT-SAGE benutzt, das mit einer Datenbank arbeitet in der die Gleichgewichtskonstanten gespeichert sind. Für diese Arbeit wurde eine optimierte Datenbank genutzt, die das Schmelzen der Ascheelemente und das Verhalten der toxischen Spurenelemente in der Schmelze mit berücksichtigt.

Die Ergebnisse der Kohle/Papierschlamm Mitverbrennung zeigten, dass die Mitverbrennung die Bildung von Alkali-Sulfaten und Alkali-Aluminium-Silikaten in der Flugasche erhöht. Dies geschieht wegen Interaktionen zwischen Alkali und Kaolin-Mineralien. Diese Interaktionen setzen Cl als HCl im Rauchgas frei. Die Größe und Konsistenz der Ca-angereicherten Agglomerate im Bett hatte keine Einfluss auf den Fluidisierungsprozess.

Die Interaktionen zwischen Alkali aus Stroh (insbesondere Kalium) und Asche-Elementen aus Papierschlamm erwiesen sich als besonders wichtig bei der Untersuchung der Kohle/Stroh/Papierschlamm Mischungen. Diese Ergebnisse können auf andere Biomassebrennstoffe erweitert werden, die hohe Alkali-Konzentrationen haben.

Die experimentellen Untersuchungen wie auch die Gleichgewichtsberechnungen zeigen, dass sich die Tendenzen zur Bettagglomeration bei der Mitverbrennung von Mischungen mit hohen Papierschlammanteilen erhöhen.

Die Gleichgewichtsberechnungen und die experimentellen Untersuchungen zur Charakterisierung von Bettagglomeraten zeigten eine gute Übereinstimmung, wenn sie anhand der berechneten Temperatur der brennenden Partikel verglichen wurden. Es zeigte sich, dass die genaue Bestimmung der Partikeltemperatur in der Wirbelschicht für korrekte Voraussagen der Bettagglomeration und der Ascheschmelzpunkte bei typischen Betriebsparametern der Wirbelschichtfeuerungsanlage sehr wichtig ist. Modellrechnungen zeigten, dass die Partikeltemperaturen während der Verbrennung bis zu 400°C über der Betttemperatur liegen. Dies gilt insbesondere für Kohlepartikel, die beim Zusammenstoß mit Stroh- und Papierschlamm-Kokspartikeln das Schmelzen von Al-, K- und Ca-Silikaten initiieren können.

Die Bildung von Feinstäuben bei der Mitverbrennung von Papierschlamm hat einen positiven Effekt auf die Emissionen von toxischen Spurenelementen, da die große Oberfläche der kleinen Partikel die Abscheidung durch chemische Reaktionen oder Kondensation erhöhte.

Die Ergebnisse von der Versuchsanlage wurde mit denen einer Untersuchungskampagne an einer großen ZWS Feuerungsanlage verglichen. Dabei wurden die gleichen Brennstoffe und Brennstoffmischungen unter ähnlichen Verbrennungsverhältnissen eingesetzt. Vergleichend wurde die chemische Zusammensetzung der verschiedenen Ascheströme charakterisiert. Unterschiede zwischen den zwei Anlagen wie die Brennkammergeometrie, das Partikelabscheidesystem sowie die Gas- und Partikel Temperatur- und Zeitgeschichte, müssten hierbei berücksichtigt werden. Die Aufteilung der Elemente Cl, K und S zwischen Bettasche,

grober und feiner Flugasche und die Anreicherung von Spurenelementen wie Cd, Pb, Mn in der feinen Flugasche war für die beiden Anlagen ähnlich.

Mono- und Mitverbrennungsuntersuchungen zeigten, dass die Anreicherung der Alkalichloride in der feinen Flugasche verstärkt wird, was zur Korrosion durch Bildung von Ablagerungen führt. Deshalb sind Untersuchungen zum Mechanismus der Cl-Einbindung erforderlich, um die Verbrennungsbedingungen optimieren zu können. Das Verhalten von Cl und die Anreicherung von Risikoelementen bei der Verbrennung der Papierschlämme mit Al-Zusätzen, wie Kaolin, Bauxit, und Kalkstein, wurde unter stationären Wirbelschicht-Bedingungen untersucht.

Die Ergebnisse für Papierschlämme wurden mit anderen schwefelfreien Biomassen und Biomasse-mischungen verglichen (Holz) indem ähnliche Untersuchungen in einer Labor-SWS Anlage durchgeführt wurden. Die Ergebnisse zeigen, dass chemische Reaktionen zwischen Al-Zusätzen und Alkalichloriden bei Wirbelschichtverbrennungsbedingungen stattfinden.

Alle Zusätze brachten Cl von der festen in die gasförmige Phase. Die Reduktion von Cl in der Flugasche ist wichtig insbesondere für kleine Partikel, die wegen Ablagerungsbildung und Korrosion sehr schädlich sein können.

Im Gegensatz zu Al-Komponenten, verringert Kalkstein die HCl-Bildung und erhöht die Cl Einbindung in die Flugasche. Cl wurde dabei aber meist in der groben Flugasche eingebunden, die wahrscheinlich weniger riskant für Feuerungsräume sind.

Der Wert dieser Studie ist mit der Frage verknüpft, ob die Resultate von der Versuchsanlage auf große Dampfkessel übertragbar sind. Ein scale-up auf industrielle Wirbelschichtdampfkessel hat sich bisher meist auf die Betrachtung hydrodynamischer Ähnlichkeiten konzentriert anstatt nach ausreichenden Verbrennungsparametern zu suchen. Das Problem wird meist erschwert, da bisher keine rigorose Annäherung in Bezug auf das Asche Verhalten angenommen worden ist. Mit den hier angewendeten neuen wissenschaftlichen Untersuchungsmethoden des Ascheverhaltens konnte gezeigt werden, dass ein gutes Potential besteht, das Ascheverhalten in Laboranlagen vorauszusagen, wenn die gleichen Bedingungen (Brennstoff, Luftverhältnisse, vergleichbare Temperatur/Zeit-Geschichte der Rauchgase) eingehalten werden.

SUMMARY

The present work analyses the ash behaviour and the environmental impact with respect to the toxic trace metals upon co-combustion of paper sludge, a waste deriving from the treatment of recovered paper, with coal and coal/biomass blends in fluidised bed combustors designed for energy production or steam generation. The study has been conducted in the framework of a European research project aiming at widening the spectrum of fuels utilised by coal-fired and coal-straw fired fluidised bed boilers, at improving the potential to use energy-containing residues, and at assessing the environmental impact of waste co-firing.

The behaviour of the ash-forming constituents when co-firing is of main interest; recently several research activities have shown that, in coal-firing designed boilers, the interactions occurring in the combustion process between the inorganic constituents of biomass and waste fuels with coal ash may cause operational disturbances, related to phenomena like slagging and fouling; as this may restrict for technical reasons the utilisation of these unconventional fuels, it is of great importance to assess the potential risk in fluidised bed boilers associated to ash deposition on heat exchangers and of bed agglomeration.

Investigations on the behaviour of toxic trace elements (like Cu, Pb, Zn, Cd) when (co) firing paper sludge are motivated by the occurrence of these metals in relevant concentration in the sludge, which may be of significant environmental and health concern.

For the first time, extensive information on the ash behaviour related to co-firing of paper sludge with coal and with coal/straw blends is reported. In this framework the question arising has been to determine whether and how the co-firing of fuels with different combustion characteristics is going to affect the ash formation and, consequently, the behaviour of the toxic trace metals. The study enlarges the current knowledge of the ash-related phenomena when co-firing those fuels whose combustion phases are not similarly structured, like coal, straw and paper sludge. Special emphasis has been given to the comparison of the experimental studies with the theoretical prediction of bed agglomeration tendencies when co-firing. Differences of physical properties between the fuels may lead to the overlapping of combustion phases and this may influence the local temperature conditions in the fluidised bed. The results of this work emphasise the importance that a correct determination of the particle temperature in a fluidised bed may have especially for the prediction of bed agglomeration phenomena and ash melting behaviour under typical operative conditions of a fluidised bed boiler.

In the present study the analysis of the mechanisms that the trace metals undergo upon combustion process and the cooling of the flue gas (roughly divided in vapourisation and

condensation) has been conducted in parallel to that of the transformations of the main ash-inorganic constituents of the fuel to which the trace metals are usually associated.

The experimental part of the work can be divided into two main sections:

- 1) Combustion test runs of paper sludge as single fuel: An extensive experimental work has been carried out at a fluidised bed test-scale facility (30 kW) to investigate the combustion behaviour of different paper mill wastes (sludge from primary mechanical separation process, and deinking sludge) fired as single fuels.
- 2) Co-combustion test runs: this is the principal part of the whole study and consists of co-combustion experiments using paper sludge as auxiliary fuel together with coal and coal/straw based blends (50/50 on an energy basis). Test runs were performed at a test-scale facility. In these blends, paper sludge replaced coal up to a share of 25 %, thus covering realistic fire-blending ratios for a near-end industrial implementation.

Performing co-combustion test runs of paper sludge with coal and coal/straw derived mainly from the interest of acquiring detailed knowledge on the combustion behaviour of these fuel blends to be fired in a CFBC 80 MWth CHP boiler, located in Greena, Denmark. The principal fuel blends of the boiler are coal or coal/straw blends (maximal 50/50 on an energy basis) but there was interest to enlarge the spectrum of the fuel blends to be fired in the boiler, and to replace the fossil fuel share.

Extensive ash sampling in different ash-output streams was the first step to allow an evaluation of the ash behaviour by means of accurate mass balances and enrichment studies. The mass balances in a BFB/CFB boiler are usually complicated from the presence of the bed material. The formation of fly ashes and bottom bed ashes (with special emphasis on bed agglomeration) has been subject of experimental parametric investigations.

Of special interest was the fate of sulphur, chlorine and of alkali elements, which may cause ash-deposit formation along the flue gas path; accumulation of alkali-based compounds may lead to bed agglomeration in the combustion chamber. The main ash-forming constituents for paper sludge are Al and Ca deriving respectively from paper fillers like Kaolin and calcite. The impact of Al/Si and Ca on the partitioning of Cl and on the enrichment of risky elements has been also subject of separated experimental investigations.

The fate of Cu, Zn, Pb, Mn, Cd upon combustion has been studied. These elements have been chosen for their high environmental and health concern; they can be highly concentrated in sludges from paper mill wastes. Information on their behaviour was obtained by studying the experimental partitioning of the toxic trace metal between bottom bed ash, fly ash (divided in a coarse and a fine fraction) and flue gas.

Valuable additional information on the behaviour of the inorganic matter and of the melting behaviour of the fuel blends of interest has been given by equilibrium calculations performed at the Combustion Research Department of Åbo Akademi University. The calculations report the formation of the stable condensed and gaseous species on a wide temperature range (400-1200°C); in this way detailed knowledge of the speciation of toxic trace metals and of the transformations of the inorganic constituents in the combustion chamber and along the flue gas path has been achieved. An extensive, specially designed, database of equilibrium constants was used within the work. The cornerstone for the work is global equilibrium analysis that simultaneously takes into consideration all chemical species, trace metals and main ash-forming constituents. The novelty of the database is that it accounts for partial melting of the ash forming elements and dissolution of the toxic trace elements in the melt.

Combustion test runs when burning paper sludge under bubbling fluidised bed conditions as single fuels have revealed the strong dependence of the combustion behaviour and ash formation on sludge properties like ash content and fibrosity. Upon combustion, paper sludge coming from primary treatment behaves differently than the much more fibrous deinking sludge; paper sludge is a much lighter fuel than deinking and tends to burn at the surface of the bed, while deinking sludge tends to burn more on the bottom; these differences are reflected on the interactions with the bed material; the release of inorganic matter leads to the formation of a light coating on the bed, without relevant risk for bed agglomeration; upon combustion of deinking sludge, on the contrary, bed agglomeration occurred and agglomerate layers formed which provoked also fluidisation instabilities.

Sintering of fine inorganic paper fillers caused the formation of fine fly ash which formed porous agglomerates: this was composed mostly from alkali-(aluminium) silicates and Ca-silicates. Deinking sludge tended to produce coarser fly ash particles than the sludge from primary treatment.

The toxic trace metals of interest were scarcely emitted in the flue gas; equilibrium calculations and leaching analysis supported the result that they are bound mostly as not leacheable forms in coarse and fine fly ashes, giving evidence of the formation of silicates-containing compounds.

Co-combustion test runs for coal/paper sludge blends have been performed under CFB conditions, coal/straw/paper sludge blends have been burned under BFB and CFB conditions and a comparison between the operative conditions has been performed.

Results of coal/paper sludge blends firing tests indicate that co-firing enhances formation of alkali sulphates and of alkali aluminium silicates in the fly ash, as a result of interaction between alkali and kaolin minerals; this provokes Cl release as HCl in the flue gas from the furnace. The size and consistence of Ca-enriched agglomerates in the bed did not provoke any disturbance in the fluidisation process.

The interaction between alkali from straw (especially K) and ash-forming constituents from paper sludge has been of particular interest in the analysis of the behaviour of the coal/straw/paper sludge blend. This study is interesting as it could be extended to other biomass fuels characterised by high alkali content and for which paper sludge represents a potential auxiliary fuel for co-firing. Experimental results and equilibrium calculations show that bed agglomeration tendencies due to enhanced melting formation are increased when co-firing blends containing higher shares of paper sludge.

Correlations have been found between the outcome of the chemical characterisation on the bed/agglomerated samples and the equilibrium analysis on the ash melting with the experimental bed temperatures profiles and with the calculated temperature of the fuel-burning particle. Theoretical calculations indicate that particle temperatures, which could be higher up to 400 °C than bed temperatures, mostly due to coal particles, may be responsible for the enhanced melting of Al, K- and Ca silicates through collisions or formation of clusters from straw or paper sludge.

It was found, through the comparison of BFB and CFB mode, that the presence of paper sludge in the blend impacted to a similar extent the fly ash formation and the composition, independently of the fluidisation mode. Fluidisation parameters (in terms of velocity and bed particle size) played, on reverse, an influencing role on the occurrence of bed agglomeration phenomena.

Under co-firing conditions, it was observed that from paper sludge mineral matter sintering phenomena, the high generation of fine fly ash from sintering phenomena for paper sludge, was seen to have a beneficial impact on the capture of the toxic trace metals, a larger surface area is provided, on which capture of vaporised species may be enhanced, either for chemical reaction or condensation phenomena.

Equilibrium calculations show that elements like Zn, Cd, Pb, Cu will form mostly silicate-based compounds for both coal-based and coal/straw based blends; therefore its environmental risk is expected to be much lower than if the elements had been present as water-soluble form. Elements of major concern are Cd and Pb due to their very high enrichment in the fine fly ash; Zn, Mn and Cu showed less evidence for vaporisation upon combustion. Trace elements were not accumulated in the bed. Dissolution of Cu, Zn, Pb in the melt occurring at typical bed temperatures (880°C) when firing coal/straw/paper sludge was predicted by the equilibrium calculations, in agreement with the high recovery in the bed for these compounds.

A comparison of the results of the test-scale facility with those obtained during a co-firing test campaign in a large-scale CFB boiler (80MWth, Midtkraft Power Plant, Greena, Denmark) has been carried out; the same blends had been fired using very similar co-firing ratios. The comparison was focused on the chemical composition of different ash streams. Dissimilarities between the two facilities related to boiler construction, ash recovery system, gas and particle temperature-time history in the combustion chamber and along the flue gas path, had to be taken into account in the study; the difficulties of performing reliable mass balances in a large-scale unit and of getting a large-scale boiler into equilibrium complicated the scale-up procedure. Similarities were found with respect to the partitioning of elements like Cl, K, S in the fly ash streams and in the enrichment of trace metals like Cd, Pb, Mn.

Single- and multi-fuel test runs raised up the issue of the capture and enrichment of alkali chlorides in the fine fly ash, which leads to formation of corrosive deposits. The behaviour of Cl and enrichment of risky elements upon combustion of paper sludge assisted by additives like kaolin and limestone under bubbling fluidised bed conditions was investigated, as these compounds are present as mineral matter constituents in the ash of the paper sludge as paper fillers; investigations on the mechanisms ruling the capture of Cl from these additives is of interest also to optimise co-firing conditions.

Other Al-based additives, like bauxite and fly ash from a stoker-fired boiler were investigated among the measures to optimise the Cl behaviour. Results obtained for paper sludge have been

compared to other low-sulfur biomass-based feedstocks (wood/bark based), according to tests performed in a BFB combustion facility similar to that used in this study. The results show evidence for the existence of reactions between aluminium-containing additives and the alkali chlorides at fluidised bed operating temperature.

Under the conditions studied, Al-compounds clearly transferred Cl from solid phase to vapor phase. It was suggested that the dominating pathway involves reaction of Al-compound with gaseous alkali chlorides in the combustion chamber produce HCl and alkali aluminum (MAI) silicates, which are then transferred mainly to coarse fly ash. The reduction of Cl concentration in fly ash effected by addition of Al compounds is significant especially for small particles, which are more harmful to the boiler furnace in terms of deposit formation and corrosion.

Limestone instead had an opposite effect to Al-compounds: it decreased HCl formation and increased Cl binding in the fly ash. However, Cl was mostly transferred to larger particles, which probably are of lower risk for the boiler.

Further investigations are necessary to extend the conclusions of the study to CFBC conditions; the extension to high- sulfur content fuels still requires to be investigated.

The study opens questions about the transferability of the results obtained in a small-scale facility to large-scale boilers. Scale-up on fluidised bed boilers has been so far concentrated mostly on hydrodynamical similarities rather than on the search of adequate combustion parameters. The issue is still much more complicated as no rigorous scale-up approach has been taken so far with respect to the ash behaviour. With the support of recent scientific investigations concerning scale-up of ash behaviour, the study shows that a good potential to predict the ash behaviour in small-scale facilities exist when adequate conditions (fuel, air ratios, flue gas temperature/time history) are respected. It is therefore believed that the phenomena described in this study will occur also in large-scale facilities operating with similar combustion parameters.

List of symbols and abbreviations

Abbreviations

AAS: Atomic Absorption Spectroscopy

BFB: bubbling fluidised bed

BFBC: bubbling fluidised bed combustor

CFB: circulating fluidised bed

CFBC: circulating fluidised bed combustor

db: dry basis

DMA: differential mobility analyser

EDX: Energy dispersive spectroscopy

ER: enrichment factor

E_{cic}/E_{fil} : ratio between enrichment factor calculated for cyclone ash and enrichment factor calculated for filter ash

EPMA: electron-probe micro analyser

ESP: Electrostatic precipitator

FB: fluidised bed

FGD: flue gas desulphurization

IC: Ionic Chromatography

IVD: Institut fuer Verfahrenstechnik und Dampfkesselwesen

LHV: low-heating value of the fuels (MJ/Kg)

LSF: large-scale facility

LPI: low-pressure impactor

KWth: thermal Kilowatt

M: atom of alkali

MWth: thermal Megawatt

MWel: electric Megawatt

PS: paper sludge

RDF: refused derived fuel

RR: recovery rate

SEM : scanning electron microscope

SCR: selective catalytic reduction

SNCR: selective non-catalytic reduction

TSF: test-scale facility (abbreviation referred to the fluidised bed combustion facility – thermal input = 30 kWth - used to perform the experimental test-runs of this study)

TFR: tube furnace reactor

wt%: weight percentage

UV: ultra-violet

VTT: Technical Research Centre of Finland

XRF- X- ray Fluorescence

XRD: X-ray diffraction

Symbols

d: particle size (μm)

d_{50} : mean particle size of a particle size distribution (μm)

Re: Reynolds number

Fr: Froude number

T: temperature ($^{\circ}\text{C}$)

P: pressure (atm)

s: solid phase

g: gas phase

l: liquid phase

1. INTRODUCTION

1.1. Waste co-combustion

One realistic option contributing to fulfil the provisions of the Kyoto Protocol, committing the European Union to achieve over the period from 2008 to 2012 an overall greenhouse gas emission reduction by 8% compared with the 1990 levels, is represented by the substitution of fossil fuels with low-carbon fuels for energy production purposes.

The use of biomass and biomass-derived waste (bio-waste) fuels, providing partial substitution of fossil fuels, has the potential to be CO₂ neutral. Biomass-derived waste (whose organic fraction comes from renewable biomass, hereinafter called “bio-waste”) meet the more general definition of waste, as wastes are processed materials that would not exist but for the intervention of man.

Energy recovery from wastes of different origin, e.g. industrial or agricultural, has become also a generally accepted alternative to disposal or incineration. Waste-to-energy is gaining more and more attention as landfill costs and environmental concern arise and, at the same time, space available for landfilling waste is diminishing, especially in densely populated areas. Along with landfill CO₂ and CH₄ emissions, potential groundwater pollution, the diminution of space available for landfilling has led to policy and legislation to increase the reuse and recycling of wastes. Legislation under preparation in the EU will prohibit landfilling of energy-containing waste. In Germany, in the framework of the Municipal Waste Management Provisions (TA Siedlungsabfall, 1993), the landfilling of any organic matter will be forbidden, at the latest by 2005. The abundance and low cost of bio-waste suggest that energy production could be a realistic alternative mode of disposal.

The concept of waste co-firing is relatively new. Due to the reliance on imported energy sources (Green Paper on the security of energy supply, 2000), the recent interest shown by the European Community in the use of wastes or dedicated biomass fuels as a strategy to reduce greenhouse gas emissions, has led an additional value to co-firing. Coal-waste co-firing has been assessed to offer an environmentally sound, economic approach to both waste remediation and energy production. Co-firing represents already an economic option, as it does not necessitate building appropriate plants; the equipment needed to handle and burn fossil fuels – especially coal- can be easily modified to accept wastes. Currently in many EU countries, the construction of new

biomass/waste fired plants with very high investment costs is viewed as a feasible option only in the medium or long term.

Consideration of political nature, such as pollution control regulations and waste minimisation rules, economics, become critical factors when choosing the waste and the amount of waste to be co-fired. For example, the availability of a certain waste in a certain region is a primary economic factor affecting fuel cost and fuel transportation.

In the list of auxiliary fuels, paper sludges and paper rejects may cover an interesting role. Under the name paper sludge it is generally understood a waste stream originating from water-treatment rejects that are separated from the mill effluent during the treatment process of (recovered) recycled paper¹. The properties of paper sludges and paper rejects differ in dependence on the stage of the treatment process, and on the process configuration.

In Europe, the Confederation of European paper industries, CEPI, in its 2000 statistical report, indicates that in 1999 more than 38 million tonnes of recovered paper and board were used as a raw material by the industry in Western Europe, with a utilisation rate of recovered paper and board of 45,1 %.

There is general agreement that recovered paper recycling is preferable to recovered paper incineration or to recovered paper landfilling, as this results in lower emissions of global warming emissions, and of most of the harmful toxic air-borne emissions, in comparison to a scenario based exclusively on a virgin fibre-based production and landfilling of recovered paper (Grieg-Gran, 1997).

The attention and the efforts of the paper industry towards a ecologically sustainable and socially desirable development related to recycling have faced growing problems of waste management. Paper rejects and sludges are generated waste material from recovered paper processing. Considering the proportions and numbers concerning the paper recycling industry, it is therefore evident, that the disposal of paper residual sludges and rejects is a problem confronting the paper industry which is compounded by the shift towards recycling. Approximately 1/3 of the waste paper volume processed in such mills becomes sludge and rejects (Göttsching et al, 1996), so that the production in western Europe is approximately 17 million tonn/y. The disposal of residual paper sludges and rejects is a problem confronting the

¹ In the EU, sludges and residues containing organic material (and therefore suitable for energy production) deriving from the recycling of recovered paper are classified as waste. In the Council Directive on waste 75/442/EEC (94/3/EC) “deinking sludges from paper recycling”, “wastes from pulp, paper and cardboard production and processing”, “fibre and paper sludge”, “rejects from paper and cardboard recycling” are inserted in the European waste catalogue.

paper industry which is compounded by the shift towards recycling. Almost paradoxically, increased recycling has provoked a significant increase of the amount of sludge being generated. Separately, the interest for energy recovery from paper sludges and rejects is growing as landfilling is becoming increasingly expensive and less viable in most of the countries. For those reasons, the use of paper sludge for energy production has encountered increased attractiveness as being a cost-effective, and an environmentally acceptable disposal method (Anthony et al, 1993; Preto et al, 1999; Torii et al, 2001). Burning paper sludges represents two sources of cost saving for a paper mill: reduced disposal costs and reduced fuel consumption for steam generation/energy production.

The option to utilise paper sludge as a co-firing (bio-waste) fuel for energy production has been recently considered in many European countries. The organic fraction in paper sludge is renewable, and therefore it does not contribute to net CO₂ emissions.

Denmark has, among the others, recently shown interest in paper sludge utilisation together with coal and coal/straw blends. In this country the strategy versus the substitution of coal with biowaste like paper sludge arises from the necessity of replacing fossil fuel with “renewable fuels” due to a CO₂-tax which obliges to find fuels cheaper than coal; straw must be used according to Danish Environmental regulations and the straw price is 3 or 4 times higher than coal and therefore it is necessary to optimise the economy of the plant.

Interest of combined utilisation of straw and paper sludge has been recently viewed in Spain for decentralised energy generation purposes.

While in the last years the efforts of fundamental research and applied combustion technology have expanded on alternative biomass and bio-waste fuels, only little information is so far available on the technical and environmental feasibility of firing paper sludge as single fuel and as additional fuel to be fired with fossil fuels, like coal, or with other biomass fuels, like straw.

Fluidised bed boilers have offered so far a feasible technological solution for the energetic utilisation of this material, as they are well suited for the combustion of wet and inhomogeneous material, mainly because the mass of the hot bed material is large in relation to the mass of the burning fuel. The low and well-controlled combustion temperature can lead to low NO_x emissions and effective sulphur capture. However, many unresolved questions are still arising, as it will be explained in the following paragraph

1.2 Objectives of the work

The present study has been conducted in the framework of a European research project aiming at widening the spectrum of fuels utilised by coal (and coal/straw)-fired fluidised bed boilers, at improving the utilisation potential of energy-containing residues, and at assessing the environmental impact of waste co-firing. The waste analysed in the study is the paper sludge. Necessity of detailed and fundamental investigations raised from the lack of knowledge of the behaviour of paper sludge upon co-firing with such coal and coal/straw based blends. In order to demonstrate the feasibility of co-firing such fuel mixtures, a special characterisation of ash behaviour was required, which allowed answering the following questions:

- Is there a significant risk associated to toxic trace metal emissions in the flue gas and particulate?
- Is there a significant risk associated to operational problems due to ash behaviour?
- How is the behaviour of paper sludge trace metals influenced by co-firing conditions?
- How is the behaviour of the main ash forming constituents influenced by co-firing?
- Which are the interactions occurring between main ash forming and trace metals when co-firing?

In the 2nd chapter a literature review is presented on the current knowledge on ash-formation and ash-related problems upon fluidised bed combustion, like bed agglomeration, and on the mechanisms of transformation of the toxic trace elements. Accent has been put on the behaviour of non-conventional solid fuels (biomass and waste). In parallel, the state of the art of the waste streams generation by the paper industry is introduced, to give emphasis on the utilisation of paper sludges and rejects as fuel for energy production purposes.

In the 3rd chapter the analytical methods and the fluidised bed combustion test-scale facility (30 KWth) are presented. A brief analysis on the experimental methodology used to investigate ash behaviour is given, including a discussion and comparison with the state of the art.

In the 4th chapter the results concerning the fuel and ash characterisation and the test runs effected at the fluidised bed combustion test-scale facility are shown; these experiments aimed at characterising the combustion behaviour of paper sludge fired as single fuel. Differences between various types of paper sludge are presented. Accent has been put on the comparison with other waste streams and in particular with deinking sludge, which had been subject of previous investigations.

In the 5th chapter the results of an experimental campaign based at assessing the impact of paper

sludge ash-forming species deriving from the paper fillers (Al-based, like kaolinite, and calcite) on the enrichment of risky elements for corrosion, like alkali chlorides, are presented. The experimental campaign is compared to a similar one, performed burning other low-sulphur biomass fuels under similar test-run conditions.

In the 6th chapter the most important results concerning the experimental co-firing campaigns are shown. Experiments under bubbling fluidised bed conditions and circulating fluidised bed conditions have been performed for co-firing of coal/straw/paper sludge. The comparison of the results of the two modes of operation is presented. This gives information on the scale-up on and the influence of the operative parameters.

In the 7th chapter the transferability of the results to large-scale plants is discussed. The experimental campaign in the test-scale facility has been put in comparison with an experimental co-firing campaign performed in the 80 MWth CFB boiler of a power plant located in Grenå, Denmark. In addition, a scale-up analysis is presented.

To validate the test-runs, an accurate methodology has been set-up to compare experimental ash partitioning with thermodynamic equilibrium calculations reporting the speciation of the main inorganic constituents and of the toxic trace metals over a wide temperature range; the results of the comparative approach are shown in different sections of the study.

2. LITERATURE REVIEW

2.1 Fluidised bed combustion: introduction

After the extensive improvements of the last few decades, fluidised bed combustion (FBC) is nowadays a mature combustion technology. In the fluidised bed combustion process, the primary combustion air is flowing upwards in the combustion chamber with a velocity high enough to reach the fluidisation of the solid particles in the flow, instead of being pulled down by gravity. When the pressure drop equals the bed weight per unit area, the bed is “suspended”, and further increase in the flow rate cease to significantly affect the pressure drop. Usually the airflow velocity is significantly higher than the minimum velocity required for fluidisation of the solid particles. The gas flow, in excess if compared to the onset of fluidisation, provides intense agitation and mixing of the bed. This provokes a separation between larger particles (which will drop back and remain in the bottom) and the finer (which will be eventually elutriated out of the combustor).

The two basic modes are bubbling and circulating fluidised bed (combustion) systems, hereafter referred by the acronyms BFBC and CFBC.

In a typical BFBC operation mode, the space above the bed (the so-called freeboard) provides ample room for the fallout of particles with terminal settling velocity less than the superficial gas velocity. If the gas flow rate is increased still further, the elutriation may become heavier, until the distinction between the bed and freeboard dissolves and the whole combustor is filled with a strongly agitated, elutriating particle bed. This mode of operation requires a hot, large cyclone, located downstream the combustor, which may recirculate the particles larger than the cyclone-cut diameter back to the bed, to maintain the bed temperature. Finer particles are released with the flue gas as fly ash. This is the operation principle for CBFC.

In industrial plants the velocity for CFBC reactors is in the range of 5-6 m/sec, for BFBC reactors, instead, it is usually 1-2 m/sec (Anthony, 1995b).

The solid inventory usually consists of quartz or natural sand, and fuel-originated ash as single particles or attached on the sand particles, and sorbents like limestone. The bed inventory is periodically removed to keep constant the pressure drop in the bed (usually 5-15 kPa). This solid inventory is forming the “bottom ash” extracted from the bottom of the bed.

Usually the operating temperature (bed temperature) of a FBC reactor is 800-880 °C. Bed particles absorb the heat generated during combustion and distribute it throughout the furnace by convection and radiation. The principal reason for the low temperature is the optimum sulphur capture: if sulphur capture is an issue to avoid too high SO₂ emissions, the combustor is

typically fed with limestone or dolomite particles which calcine and then fix SO_2 in the temperature range of 800-900 °C, which reacts to form CaSO_4 (Liang et al, 1991). This low-temperature range leads to a limited ash softening; a further advantage that follows out is also that virtually no thermal NO_x is produced.

2.2 Fluidised bed combustion of biomass/waste

Fluidised bed combustion technology allows great fuel flexibility. Due to the fact that the fuel is present in the combustor in low percentages with respect to the total solid inventory, and that is therefore burned in the mass of a thermally inert bed material, in practice different kinds of solid, liquid and gaseous fuels are burned under FBC conditions. By means of FBC boilers, wastes can be burned more effectively at lower temperatures than the conventional technologies (Anthony, 1995b). The success of FBC technology in destroying special wastes is related to the highly isothermal conditions and to the higher degree of mixing compared to many conventional combustion systems (Anthony, 1995b). One of the advantages of the FBC technology is the relative scarce preparation of the fuels in comparison to other combustion systems: the intense motion of the fluidised bed makes it possible to combust a wide range of fuels having different sizes.

There are nowadays many examples of FB boilers applied for burning biomass. For example, as far as the combustion of agricultural residues concern, plants in a capacity up to 30 MW and fired with almond shells, cotton stalks went in operation in the USA since the begin of the 90's.

Waste combustion in FB boilers from industrial production is also reported (Anthony, 1995b; Werther et al, 2000; Leckner et al, 2001b; Anthony et al, 1993; Anderl et al., 2001, Gulyurtlu et al, 2001). In Germany 17 bubbling fluidised systems are used for sewage sludge incineration.

Although the capital cost of the FBC technology is a major issue, the technology becomes attractive for fuels dictating that flue gas desulphurisation (FGD) or selective (non) catalytic reactors (SCR/SNCR) must be employed.

The smallest FBC plants known are of 1 MWth size to heat apartment blocks and small factories, while the largest applications are of the size of 250 MWel (Gardanne, France, provided by Electricité de France). The market is up to now dominated by FB boilers of 20-25 MWel and CFB boilers for various designs of larger units.

2.3 Waste paper processing plants - Paper sludge and paper rejects production

Figure 1 shows a typical scheme of waste paper processing coming from graphic papers (not comprising the deinking section). Each waste paper processing unit of a paper mill is a system of different units of operation, being mostly governed by the recovered paper grade(s) and the paper produced. Usually waste paper processing is based primarily on a series of mechanical operations aiming at

- 1) Formation of single fibres (slushing) which may eventually undergo successive fractionation;
- 2) Cleaning and screening for removal of impurities;
- 3) Dewatering and thickening. This process may be supported by a parallel/successive series of chemical stages, among them:
- 4) Deinking (aiming at the removal of inks but also stickies and other impurities);
- 5) Bleaching.

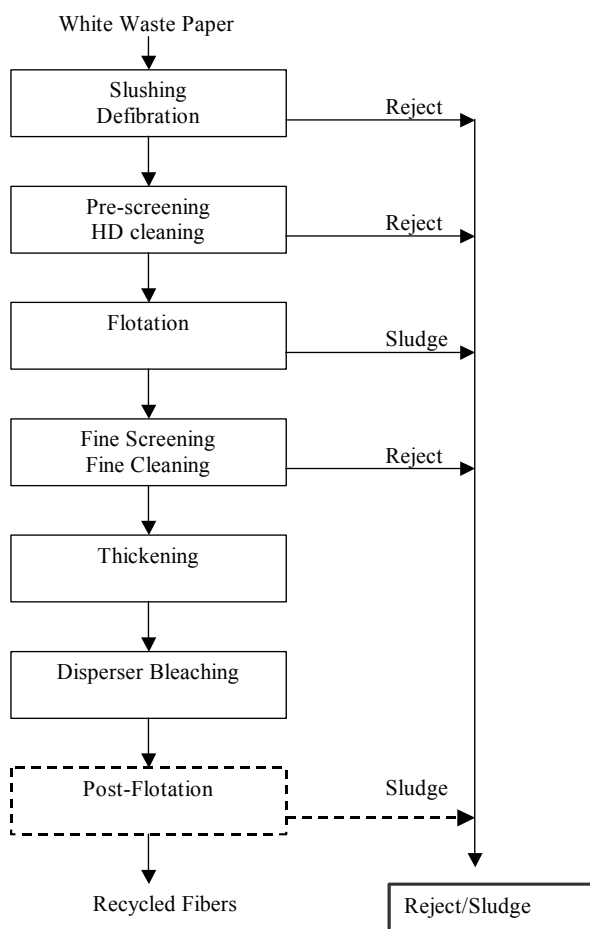


Figure 1 Scheme of waste paper processing (Göttsching et al., 1996)

Waste paper processing plants have individual designs in terms of their layout and equipment, depending on the type of paper that has to be produced; the plant may also include sophisticated systems of screening and cleaning cascades. From each stage of the process a distinct reject/sludge type (Göttsching et al., 1996) is produced; the main waste streams being - according to the preparation stage:

- A) Rejects,
- B) clarifier sludge,
- C) deinking sludge.

Rejects derive usually from cleaning and screening processes, from mechanical preparation of recovered paper: sources of rejects are slushing

and, cleaning, pre-screening and fine screening (LAGA, 1995).

Sludge derives from more sophisticated chemical-mechanical, biological, deinking upgrading processes and from wastewater treatment plant, (LAGA, 1995). **Clarifier sludge** and **biological sludge** derive from the respective wastewater treatment stages; typically this corresponds also to the division between primary and secondary sludge. Primary sludge is characterised by coarser particles, high fibre concentration; secondary sludge, instead, from less fibre concentration and paste-like appearance. Both are usually very wet.

Deinking sludge derives from deinking treatment process, which swells the fibres and loosens the ink particles and coating materials. Peroxides and surfactants are usually added to bleach the fibres and disperse the ink particles. The ink particles are removed as foam and – together with coating material, rejects and water- form what is commonly called “deinking sludge” (Latva Somppi et al., 1994).

2.4 Sludge properties as a fuel

The composition of these wastes usually varies depending on the type of raw material used and the number and type of cleaning and screening stages applied. For energy production’s purposes, it is usually not economically viable to utilise the waste streams separately, hence they are typically mixed together. This makes the characterisation of the fuel properties still more difficult.

Table 1 illustrates the composition of different sludge and rejects types in terms of proximate analysis (moisture, ash and organic matter content), as taken out from literature.

As it can be observed, sludges and rejects are characterised by different moisture and ash content. This affects the heating value and, therefore, the possibility of being fired as a single fuel or to be used as an auxiliary fuel. For some types of sludges the combustion is not self-sustaining and the support of an additional fuel -like coal, wood/bark- (Gyllenhammer, 1998; Vayda et al, 1993;) is required. Usually a dry combustible matter content of 45 to 60 % is required for the autogeneous combustion of sludge (Göttsching et al., 1996). Experiences of burning paper mill sludge with a maximal value of 43 % moisture have been reported (Gyllenhamer, 1998)

Dewatering of the sludge is the most important issue to decide how much sludge can be burned in a boiler. In some cases (Grieg-grahan et al, 1997) it may be economic to dry sludges (instead of deponating) in order to get advantages of the energetic benefits associated to sludge combustion.

Deinking sludge properties are better defined than those from other sludge and rejects types. Deinking sludge has usually a high ash and moisture content. Rejects of waste paper processing are usually composed of various material such as wooden pieces, metals, glass, stickies, etc; the not negligible share of plastic material is a reason for the high chlorine content of the rejects and for their high calorific values (LHV generally higher than 20 MJ/kg), which let them particularly suitable for energy production. So far paper rejects have been mostly disposed by landfilling. This was due to the danger of formation of dioxines and furans upon combustion. Various studies and measurements campaigns in FBC boilers demonstrate that nowadays dioxin emission from modern incinerators are too low to present any significant risk (Vayda et al, 1993; Anthony, 1995).

	Moisture (wt%)	Organic matter (wt%)	Ash (wt%)	Reference
Biological Clarifier sludge	12	40	48	Zhao et al, 1999
	65	18	17	
	64	26	10	Vahda et al, 1993
	55	32	13	Vahda et al, 1993
	12	35	53	Katzenberger et al., 1999
	76	15	9	Preto et al, 1999
	23	12	65	Göttsching et al, 1996
	34	23	43	
	10	70	20	Holbert et al, 1998
	35	30	35	Gyllenhammar et al, 1998
	45	5	50	
57	23	20		
Deinking sludge	25	10	65	Biermann et al, 1999
	45	10	45	Preto et al, 1999
	50	25	25	
	54	30	16	Göttsching et al, 1996
	62	33	5	
	12	38	50	PTS Bericht, 1997
50	15	35	ECSC project n7220-PR, 1998	
Rejects	45	15	40	Göttsching et al, 1996
	15	75	10	
	12,5	78	9,5	
	8,5	83	8,5	
	11,5	77,9	10,6	

Table 1: Paper sludge composition

A typical range for nitrogen and sulphur content of paper sludges and rejects is shown in **Table 2**. The nitrogen and the sulphur content of paper mill sludge are comparable to that of other biomass fuels like wood and straw, which are generally low in comparison to a bituminous coal.

Mineral matter from paper rejects and different kind of paper sludges consists of kaolin minerals, ($Al_2O_3 \cdot SiO_2 \cdot H_2O$) and calcium carbonate ($CaCO_3$, used to provide a light-scattering surface).

Paper sludge Ca content is usually high, and mechanisms of self-absorption of sulphur due to high amount of CaCO_3 in the ash of the waste may occur, thus enhancing sulphur capture.

In addition, other components like talc ($3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$), barium sulphate (BaSO_4), zinc oxide (ZnO) may be present in small and variable percentages; small amounts of titanium dioxide (TiO_2 , used to provide brightness and opacity to the paper sheet) and other fillers or pigments deriving from the paper production process may be also present. Na (under the form of sodium hydroxyde or sodium silicate) is usually added as deinking agent (Latva Somppi, et al 1994; Douglas et al., 1994). In some cases alum ($\text{K}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot \text{SO}_4$), soluble in water, is used as a sizing agent to retain the other additives in the paper.

Table 2 gives an example of the wide variation range of toxic trace metal content in the sludges. Trace elements originate mostly from recycled paper and clay additives. Cd, Cu and Ni mostly come from recycled paper, while Cr and Pb originated mostly from clay or from printing inks (Göttsching et al, 1996). Sludge concentrations of lead chromate might be high. Heavy metals may originate also from contamination with other substances during recycling process. The toxic trace metal concentration in a sludge depends also on the geographical origin: clays from Germany have usually a higher Pb content than other clays, whereas Cr content of North American carbonates is usually higher than that of carbonates from Europe. Cu content of deinking sludge is mainly based on phtalocyano compounds.

Hg content is very low in all the types of sludge and rejects, being of the same range of the typical concentration measured for bituminous coals. The trace metals content of deinking sludge is usually the highest among the various types of sludge, as pigments remain typically in deinking sludge in high concentrations (Göttsching et al, 1996). Their amount may be comparable with other wastes like sewage sludge.

	Biological (1)	Clarificatio n (2)	Deinking I (1)	Mixed I (1)	Denking II (2)	Rejects I (1)	Rejects II (1)	Mixed II (1)	Bark (3)	Sewage (3)	Polish Coal (3)
Hg	0,16-3,3	0,1-1,1	0,1-0,89	0,11-0,25	0,05	0,05	0,05	0,04	<0,05	1,86	0,1
Mn					72			670	334	256	98
Cd	0,15-9,1	0,01-0,98	0,02-1,5	0,08-1,1	<2	0,25	0,45	0,4	<2	2,7	0,1
Pb	10,8-394	10-210	0,5-79,4	14,0-93	4,5	35	42	85-225	<5	40	35
Zn	89,7-2350	6,4-460	34,2-1,320	84,6-320	80			440	2		440-494
Cu	33,6-494	19,9-195	64,2-345	18-206	2			270-360	2	322	52
As											
Cr	5,8-116	8,8-903	4,8-96,6	12,9-311	26			106-112	11	96	12
Ni	<10-247	<10-63,5	<10-31,3	<10-17	6,5			50-60	5	200	60
S	0,3-1,3	<0,1-0,2	0,06-0,12	0,05-0,24	0,08	0,05-0,18			0,05	1,98	0,78
Cl	0,02-0,11	0,39-21,1	1,54-14,9	0,42-16	0,11	0,01-6,1			0,03	0,08	0,09
N	0,91-8,1	0,2-0,92	0,16-0,51	0,34-1,88	0,32				0,4	3,15	0,58

Table 2: Typical trace metal concentrations in paper sludges and other fuels (1): Göttsching et al, 1996, (2) ECSC project n7220-PR-087, 1st year report; (3) Bark- Sewage- Polish Coal: Aho et al., 2001

2.5 State of the art of paper sludge combustion

Paper sludge co-firing finds nowadays application in boilers supplying energy/steam in the paper mills. Utilisation of paper sludge as auxiliary fuel with the wood/bark waste of the paper mill has been widely reported. (Latva-Somppi, 1998). This represents a “sustainable” disposal way, as the fuel transportation outside the plant is avoided.

In the previous decade the grate firing was the favourable technology for burning paper sludge; but recently FBC combustion technology started to dominate, due to its fuel flexibility, to advanced concepts of system control (for example by means of flue gas recycle), and to its environmental advantages associated to the low emissions. Nowadays generally most of the CFB/BFB boilers operating in the pulp & paper industry are fired with different kinds of wood wastes and bark, and recently the boilers have been re-adapted to fire sludge, thus saving in the costs for energy production and avoiding the disposal of this waste material.

Up to the mid of the last decade, in the US and Canada the technical, economical and environmental feasibility of the thermal treatment of paper mill sludge in FBC boilers had been addressed both on test-scale and on an industrial-scale level (Anthony et al, 1993; Preto et al, 1999). Literature had focused mainly on the technical feasibility of sludge combustion and on the principal polluting emissions (NO_x, SO₂). Previous work had been concentrated on combustion efficiency in terms of CO and other toxic hydrocarbon compounds (dioxins, chlorinated compounds, etc.), too.

When firing paper sludges in FBC boilers, a further treatment to achieve low NO_x and SO_x (Anthony et al, 1993; Preto et al, 1999) is not required, due to the low fuel-S and fuel-N contents. The mechanisms of reduction of nitrogen onto the char may be, however, absent with paper sludges, as the volatile combustion is dominating, thus enhancing the total fraction of fuel nitrogen converted to NO/N₂O (Anthony et al, 1997). Co-combustion of paper sludges with bark/wood gets advantage of the CaO from the fuels and to give high sulphur retention (Vayda et al, 1993).

In the last years effort has been done in Sweden to co-fire sludges with the typical fuels of paper mill industry, i.e. wood and bark. The tax on sludge deponating imposed by the Swedish authorities has obliged the pulp-and paper mill industries to search for alternative solutions for sludge disposal. In Sweden CFB and BFB boilers fire sludge in bark-fired boilers with a maximal share of sludge fired of 65 %, with typical values around 20-30 % (mass basis). Even a reduction

of the water content up to 15 % will be economical in saving the costs for deponating (Gyllenhamer et al, 1999).

Problems of sludge utilisation for co-firing with bark have been reported as:

- too much water in the sludge gives difficulties in keeping the boiler load
- too big amount may sinter in the fuel bed or in the ash handling system
- limitations in capacity of ash handling systems.

Successful operating experiences have been reported upon a fluidised bed combustion boiler in France (44 MWel , with steam data 19,4 kg/s; 25 bar; 225 °C- saturated), burning a variety of fuels including a high moisture content paper sludges (up to 30 % on an energy basis), together with wood waste and natural gas (Vayda et al, 1993). The boiler operates with a high staging degree of the combustion air, operated with secondary and tertiary air.

Projects of fluidised boilers firing coal and paper sludge are currently being implemented.

In China, Austrian Energy provides currently CFB boilers burning bituminous coal and various paper sludges from paper mill plants. The boilers are planned to burn sludge up to 100 tonn/day -steam data : 241 t/h; 125 bar; 538 °C-. (Zhao et al, 1999 ; Katzenberger et.al, 1999).

In Japan, Mitsubishi Heavy Industries, Ltd., has constructed a paper sludge and coal co-fired BFB boiler, which is now under successful commercial operation. The sludge energy input is approximately 45%. (Tori et al, 2001). The paper sludge mass input is 240 dry ton /day.

UPM's Caledonian Paper has a project aiming at enlarging the spectrum of boiler currently firing coal, and maximum share of 25 % bark and 5 % clarifier sludge on an energy basis. The objective is to increase the share of paper sludge (clarifier sludge) and other waste process streams (ECSC project 7220-PR-087).

Ahlstrom PyroPower had projects in North America involving large boilers co-fired with coal (Anthony, 1995b) and using sludge as secondary fuel. Riley-Stoker Corporation is exploring this market and has recently completed an extensive series of pilot-scale CFBC co-firing pulp sludges and coal. At least 6 new units at various stages of development in Canada have been reported (Anthony, 1997).

2.6 Ash formation upon fluidised bed combustion of biomass/waste

The behaviour of the ash-forming constituents upon combustion has become one area in which the development and optimisation of the FBC technology is concentrated.

Ash-related problems arise from the tendency of some ashes to adhere to surfaces (Raask, 1985; Anthony et al, 1995a; Baxter et al, 1998); ash deposit growth on heat exchanger surfaces (slagging in the combustion chamber and fouling in the convective pass) causes reduction in the heat transfer and promotes corrosion of the heat exchange material.

Bed agglomeration may decrease the heat transfer in the bed, resulting in poor conversion efficiency and in the worst case to defluidisation and unscheduled plant- shutdown (Salour et al, 1993; Skrifvars et al, 1997; Grubor et al., 1995; Lin et al, 1997; Manzoori, 1994; Natarajan et al, 1998). Defluidisation may occur in the worst case when the gas flow is not anymore sufficient to sustain the hold-up of the new grown-up particles.

In boilers designed for coal-firing, the interactions occurring during the combustion process between the inorganic components of biomass and waste fuels with coal ash may cause operational disturbances; as this may restrict for technical reasons the utilisation of these unconventional fuels, it is of great importance to assess the potential risk in fluidised bed boilers associated to ash deposition on heat exchanger and of bed agglomeration. Sludge is an unusual fuel and boiler operation can be disturbed by ash-related problem.

The investigations concerning the ash behaviour upon biomass/waste (co)-combustion have chronologically and methodologically followed the studies related to coal combustion, which had been performed in the last decades (Quann and Sarofim, 1982).

The form of occurrence of the ash-forming species in the fuel influences their transformations paths during combustion. The inorganic matter in fuels may be naturally occurring or added to the fuel through geologic or processing steps (Linak et al, 1993; Sarofim et al, 1993). One classification of the ash-forming metals is that they can be chemically bound to the organic fuel matrix (**inherent mineral matter**), or dispersed as mineral crystallites (**included mineral matter**, typically alumino-silicates, carbonates, sulphides) or in completely extraneous and distinct particles from those containing combustible parts (**excluded mineral matter**). High-rank coals contain most of the ash-forming species as minerals like silicates, carbonates, sulfides and oxides. In low-rank coals (like lignite), and in biomass fuels, the inorganic constituents are generally linked to the organic material, whose share increases with decreasing the fuel rank due to the increased oxygen content (Raask, 1985; Nordin, 1994).

Ash formation is subject of the chemical and physical process that the fuel undergoes during the combustion process.

The combustion phases may be briefly summarised in:

- drying of moisture;
- devolatilisation of the volatile organic material
- flame combustion of the devolatilised compounds;
- burning of char.

Fluidised bed combustion is characterised by lower temperatures, larger particle size, and longer residence times than pulverised fuel combustion, which is expected to have a strong influence on the behaviour of ash.

A mechanistic model for ash formation during biomass combustion has been developed by Lind et al. (1998). A schema of this model is shown in **Figure 2**. The mechanisms of ash formation are usually divided into two groups:

- **residual ash formation** (via coalescence)
- **fine particle formation** (via volatilisation/condensation).

The first involves the supermicron range and the second both the submicron and the supermicron range (Quann, 1990, Sarofim and Helble, 1993; Quann and Sarofim, 1982).

A fraction of the inorganic matter (here called “ash” for simplicity) is volatilised and released into the gas phase. The characteristics of the volatilised ash fraction depend on the fuel properties, on the combustion temperature, and on the gas atmosphere. Ash transformation takes place usually during char oxidation, when the particle temperature is usually very high; under FBC conditions the particle temperature may exceed the bed temperatures by more than 600 K, depending on the particle size and on the oxygen concentration (Joutsenoia, 1998; Winter, 1997).

The physical form of minerals has a major effect on the vaporisation of the refractory elements. Excluded mineral matter is expected to be less prone to vaporisation. Silicates structures, typical for coal, are not prone to volatilise.

Fuels, like biomass, whose ash-forming species are bound in the organic structure, will also produce volatilised ash, especially alkali-enriched, as several experiments in lab-scale FBC have showed (Manzoori et al., 1992; Valmari, 2000, French and Milne, 1994; Dayton et al., 1995).

Depending on the molar ratio alkali/chlorine, alkali release mechanisms from biomass may also involve volatilisation at typical FB temperatures, followed by subsequent condensation of MCl and/or MOH. (Valmari, 2000). Volatilisation of alkali occurs mostly during the char oxidation stage and it is scarcely influenced by combustion temperature (French and Milne, 1994) in the

temperature range 800°C- 1110°C.

Depending on the time/temperature history of the gas and fuel particles properties, and on the combustion environment, volatilisation phenomena can lead to the formation of submicrometer aerosol particles. These particles can be hardly captured by conventional particulate removal system. The mechanisms of **aerosol** formation basically consist of the following steps (Linak et al, 1993):

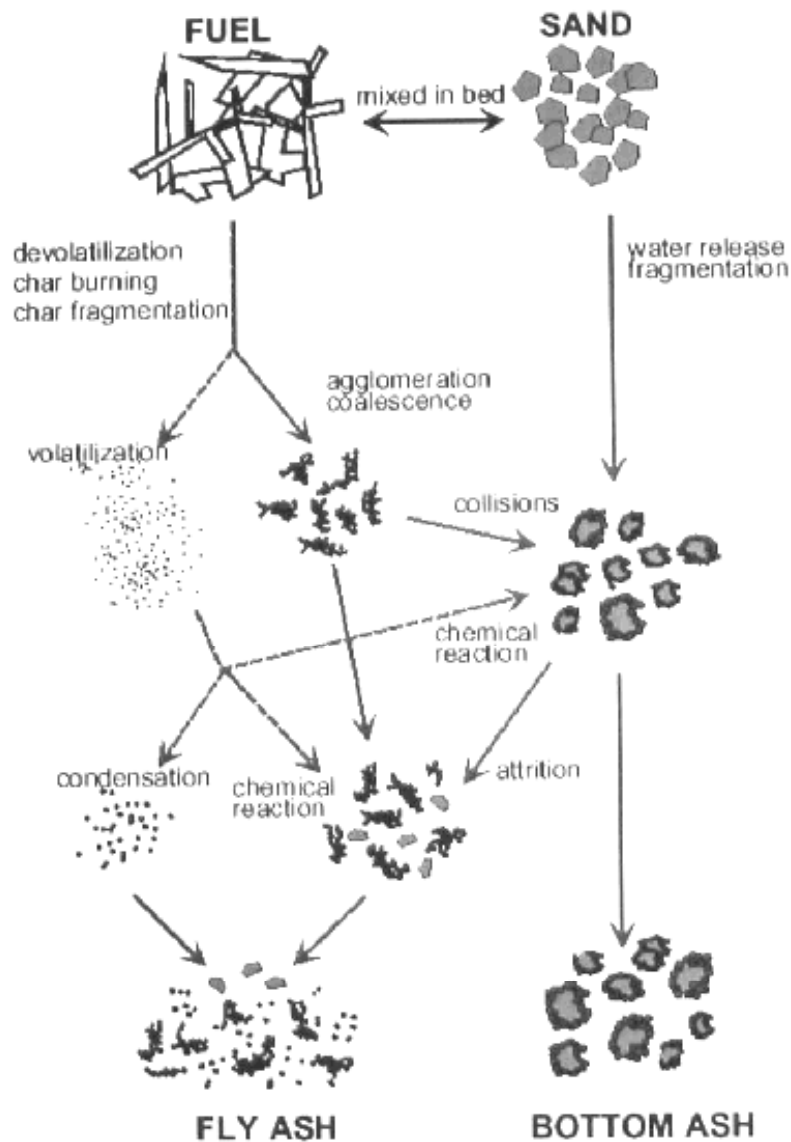


Figure 2: Model for ash formation under fluidised bed combustion (Lind, 1999)

- a) **nucleation**, when the particles are formed from a supersaturated gas;
- b) **condensation**, when the particles continue to grow, and new material will condense on the

particle surface, thus changing the particle size distribution;

- c) **coagulation**, which reduces the total number of particles in the flue gas, due to particle-to-particle collision and adhesion, while conserving the total volume (or mass) of particles, but changing the particle size distribution.

The volatilised ash fraction may form new particles in the boundary layer of the burning char particles via nucleation. Nucleation is induced when the volatile metals in forms of suboxides - usually occurring upon coal combustion-, (Quann et al, 1982), chlorides or sulfates, (Valmari, 2000; Lind, 1999) are transported into the bulk gas conditions of the furnace. Silicate minerals are not expected to generate significant amount of submicron particles (Raask, 1985).

Gaseous species may also condense on the ash structure of supermicron particles. This mechanism is called **heterogeneous condensation**. Chemical reactions also incorporate gaseous species in both size modes. (Latva-Somppi, 1998; Haynes et al., 1982).

Residual ash includes usually particles that do not undergo volatilisation during the combustion process (Quann et al, 1990; Baxter et al., 1997). The residual ash particle size may be increased by coalescence of mineral inclusions, or addition of atomically dispersed elements to existing particles on the char surface.

A very important mechanism associated to ash-formation is **sintering**. This name defines a thermal treatment for bonding particles into a solid structure via mass transport, occurring on a solid, liquid or gaseous phase. Sintering is associated to fusion and melting of the ash particles during combustion, occurring when particle temperatures are high enough to provoke their (partial) melting (Latva-Somppi, 1998).

In FB boilers, fuel particles interactions with bed material -usually sand, or limestone in case of high-sulphur content fuels¹ - invest physical transformations of the ash-forming constituents (Lyngfelt, 1998; Anthony, 1999). Collisions of the fuel particles with the bed material affect the size of the ash, and the formation of fines (Shamlou et al., 1990). Collision leads to deposition of non-volatile elements on the bed material, too. (Latva-Somppi, 1998; Manzoori, 1994).

Interactions with the bed material may be also of chemical nature: condensation of volatilised inorganic components (like K), and chemical reactions (formation of K-silicates for example) may also occur (Valmari, 2000).

¹ For biomass, generally low-sulphur fuels, the utilisation of CaCO₃ is minimal, but it can be relevant for co-combustion with coal.

A very important area of study of ash behaviour concerns **fragmentation** phenomena of fuel particles. These phenomena are of particular interest upon FB combustion. Fragmentation phenomena may be caused by shock and stress during devolatilisation, - primary fragmentation- generally affecting the high-volatile fuels, or may occur during breaking up of the char structure- secondary fragmentation, or during the end of combustion phase- percolation. Of particular importance is the **attrition by abrasion**, which is the release of the fines from the particle surface due to the wearing in the bed (Salatino et al, 2000). Attrition, or mechanical fragmentation may play an important role for coal. All these phenomena influence the ash formation by affecting the fuel particle size, and the fuel particle temperature. The relevance of attrition phenomena is highly emphasised in the case of high-volatile fuels (Chirone et al., 1997), due to the propensity of such fuels upon devolatilisation to produce highly porous, friable chars, and to generate a multitude of fragments of small size. In the case of wood, char combustion via generation of fine char by attrition is dominating (Chirone et al., 1997). In a CFB combustor, due to the higher fluidisation velocities, the generation rate of fines is one order of magnitude higher than in a BFB combustor (Arena, 1990). It is expected that, due to its very high porosity, the generation of char fines for paper sludge may be relevant.

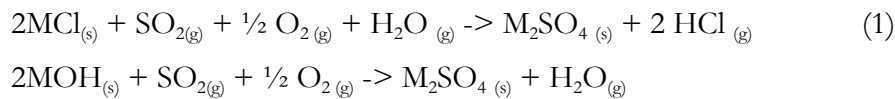
We can state that in a FB boiler, **bottom ash** is formed by residual, coarse ash particles, which remain in the bed (usually larger than 100-300 μm); **fly ash**, on the contrary, is usually formed both by residual ash that is entrained by the flue gas from the bed (typically after fragmentation, smaller than 100 μm), and finer particles formed mainly via condensation (with a particle size < 10 μm). The resulting fly ash particle size distribution is bimodal, resulting in a coarse and a fine mode. In a CFB fly ash usually includes recirculated bed material particles that have been fragmented into a very small size.

2.6.1 Alkali reactions and phenomena of fouling/corrosion for biomass fluidised bed combustion

In dependence on the specific combustion operative parameters, and on the ash composition, the ash particles formed during combustion may attach to the heat exchanger tubes on the furnace walls and in the flue gas channel. If the particle layer on the heat exchanger tube grows thick, it will reduce the heat transfer from the flue gas to the tubes, thus decreasing the efficiency to the boiler. Soot blowing is used to remove the particle layer from the tubes, but if it grows strong and tenacious, it cannot be removed by usual means.

Sub micron (aerosol) fly ash particles with high Cl content tend to form corrosive deposits on superheaters (Valmari, 2000). Hot superheater tubes are sensitive to Cl corrosion at $T > 470\text{ }^{\circ}\text{C}$, which means that Cl deposition is a risk to high-steam value power plants. Small particles are usually more enriched than larger particles in water-soluble alkali chlorides (Valmari et al., 1999a). These chlorides are partly transferred to the finest particles by condensation.

Alkali vapours released under the form of chlorides and hydroxides are subjected to chemical transformations in the combustion chamber and in the convective pass. When a low-sulfur content biomass fuel is co-fired with feedstocks of high sulphur content, Cl may react to form HCl through the sulphation reactions occurring between SO_2 and alkali chlorides (Christiansen et al, 1998; Christiansen et al, 1996; Robinson et al, 1998; Nielsen et al, 2000; Iisa et al, 1999). Reactions involving the formation of alkali sulphates can be summarized as follows:



Where M is Na or K

There is no general agreement whether the sulphation reaction occurs with vaporised or solid chlorides (Nielsen et al, 2000; Iisa et al, 1999). Studies indicate that the reactions are thermodynamically favoured at fluidised bed combustion temperatures (Halstead et al., 1969).

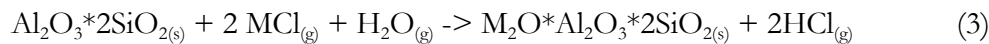
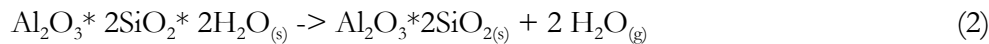
Corrosion problems due to corrosive compounds like chlorides and sulfates are of great risk for furnaces. According to thermodynamic calculations, alkali chlorides condense at about 600°C , typical temperature of a convective pass. Condensed alkali chlorides have a much longer interaction time with the steel surface than gaseous chloride compounds, as the deposited ash may wait 1-2 days for soot blowing and yet the tenacious part may not be removed.

Straw is one typical example of high-alkali, high-chlorine content biomass. Like other herbaceous fuels, its high Cl content is associated to the amount of Cl present in the nutrients. High concentrations of volatile alkali metals and Cl resulted in severe ash-related problems (Nordin, 1994; Baxter et al, 1998; Sander et al, 1997; Evald, 2000).

Hansen et al. (1995) measured alkali concentrations in a 20 MWel CFB boiler firing coal and straw, for a duration time of 10 weeks. The measurements conducted in the riser and in the pre-separator superheater section, showed a significant enrichment in alkali, S and Cl. On this basis, the authors motivated the occurrence of the fouling and slagging essentially by means of the condensation of the alkali sulfates and chlorides.

2.6.2 Cl behaviour during combustion: the influence of Al-based additives

Interactions of alkali chlorides with some of the major ash forming elements (Si, Al) may affect the fate of chlorine inside a FB boiler, influencing its partitioning between gas and solid phases. Reactions between alkali chlorides and aluminium silicates can release HCl according to the following mechanisms (Scandrett et al, 1984; Jeffers et al, 1999, Punjak et al, 1988):



Where M is Na or K

Thermodynamic calculations (Scandrett et al., 1984) show that reaction (3) is strongly favoured at FBC temperatures, while it becomes less favourable at higher temperatures. These reactions have been so far extensively investigated, the main focus of the investigation being, however, the alkali vapours-removal, i.e., the effectiveness of transforming $\text{MCl}_{(g)}$ into solid alkali phases (Scandrett, 1984); less information on HCl behaviour is known, and on the characteristics of the ash residual substrate. Knowledge of these reactions has been so far based on lab-scale experiments in fixed-bed reactors, performed under simulated flue gas atmosphere (800-1000°C). Focus of the experimental investigations is the alkali capture rate, determined by means of microgravimetry analysing the sorbent weight variation rate (Punjak, 1988).

The effectiveness of these „getter“ materials is strongly dependent on the process temperature, on physical properties of the sorbents like particle size and porosity, and on process variables like pressure and chemical composition of the flue gas. The crystalline structures of the additives influence the rate and the mechanism of alkali capture (Uberoi et al., 1990a). Aluminium compounds may bind alkalies and release HCl via mechanisms that do not include the contribution of silicates. Activated bauxite may react at typical fluidised bed combustion temperatures (e.g. 870 °C) with alkali vapours in the following way



Reaction (4) produces HCl and alkali aluminium oxide, which is more water-soluble than the alkali aluminium silicates.

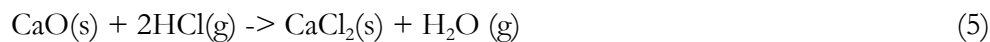
However, kaolinite binds alkalies clearly more effectively than bauxite, which shows the importance of reaction 3 for alkali capture.

Recent investigations have explored the influence of aluminium silicates on alkali retention to solid phases when co-firing coal and biomass at entrained-flow combustion conditions (Dayton et al, 2000) and in FB combustors burning brown and bituminous coal (Gottwald, 1998). To the author's knowledge, no extensive results have been reported on the impact of aluminium-based additive on Cl recovery under FB conditions; little information is available concerning biomass combustion.

2.6.3 The influence of Ca-based additives

The influence of limestone on Cl retention under BFB combustion conditions has been experimentally investigated both under simulated flue-gas atmosphere, and in small-scale FB combustion reactors. Most studies on the impact of limestone on chlorine behaviour have been carried out at high HCl and high SO₂ concentrations, focusing on both dechlorination and desulphurization efficiency (Bu et al, 1999; Matzukata et al, 1996; Liang et al, 1991). Findings suggest that HCl may be effectively retained by limestone and that SO₂ absorption is increased in the presence of HCl.

Limestone is proposed to remove gaseous Cl according to the following path:



Thermodynamic calculations have shown (Matzukata et al, 1996) that dechlorination reactions are favoured at low temperature (600 °C), at high HCl and low H₂O flue gas concentrations. Recent works (Liu et al, 2000; Xie et al, 2000) confirm that the reaction between CaO and HCl may occur at the low temperatures conditions (550-700 °C) existing after the freeboard in the flue gas path.

Few results are available on the interactions of limestone and chlorine during (co)-firing of biomass and waste; the interaction with other ash-forming constituents has been so far poorly investigated.

2.7 Bed agglomeration mechanisms upon biomass combustion

As previously described, in the presence of a bed material, easily released ash-forming metals would preferentially condense on the bed particles surfaces rather than form sub-micron-sized droplets, or directly in the flue gas. This condensation gives rise to a **coating** on the bed surface. For some fuels, like low-rank coals the coating may be due to ash transfer to the surface of the bed particles occurred by collision between sand and burning char particles (Manzoori, 1994). In dependence on the chemical composition and the bed/particle temperature, the coating may cause the initiation of the bed agglomeration by means of the formation of a sticky melt gluing the bed particles together (Skrifvars, 1998a).

Skrifvars identified three different mechanisms responsible for bed agglomeration in FB boilers:

- **partial melting.** Partial melting of the coating cause sintering through the appearance of a liquid phase in the ash particles. The amount of liquid phase controls the stickiness of the particles, and if it is great enough, agglomeration may occur. It takes typically place in the presence of ash with a high content of ionic salts. Non-viscous melt has been identified when burning high-sulphur lignites (Manzoori, 1994).
- partial melting with a **viscous liquid** Partial melting with a viscous liquid or viscous flow sintering is a mechanism occurring, for example, in silicate systems. The viscosity of the liquid phase controls the neck formation. Viscosity is a function of both chemical composition and temperature (Senior et al., 1995), these factors controlling viscous flow melting.
- **chemical reaction.** Chemical reactions between the reactive gas and the bed particles, causing the formation of a new compound forming necks between the particles, have initiated agglomeration process when using limestone as a bed material (Anthony, 1995).

Operating with biomass, the viscous flow mechanism is considered to be the predominant. The onset of sintering is due to formation of a liquid phase from the lowest melting point components. The interaction is typically occurring between alkali and alkaline earth with the other minerals present. Adhesive efficiency of the ash particles increases significantly with an increase in temperature due to a decrease in the viscosity of the molten phase of ash.

Recent results (Öhman, 2000) have addressed the responsibility for bed agglomeration during biomass combustion to the formation of enriched K-Ca-silicates; the melting behavior of these coated structure has been found to be strongly dependent on the potassium content.

Straw combustion experiments in a FB lab-scale combustion reactor (Lin et al., 1997) showed that the rate of agglomeration increases with higher combustion temperatures. The time

interval before agglomeration occurred strongly decreased as the bed temperature was increased from 800°C to 950°C.

At low temperature, defluidisation is caused by the growth of a defluidisation layer by increasing the amount of the agglomerates. When the particles begin to agglomerate during combustion, a multi-size particle system is formed, which tends to segregate with bigger and heavier particles at the bottom. When the number of the agglomerates reaches a level higher than a critical one, segregation will start and a layer of defluidized agglomerates will be formed. When agglomerates of particles exceed a critical dimension, the degree of mixing is reduced, and higher temperatures will be reached locally, resulting in further agglomeration, completing eventually bed defluidization through severe viscous flow sintering.

On the contrary, at high bed temperatures, enhanced melting may abruptly occur, and the particles may abruptly become very sticky and immediately glue together.

Combustion experiments of hazelnut-shells performed by varying the bed temperature in a 30 kWth BFBC facility have revealed and confirmed the occurrence of the two different defluidisation paths (Vivarelli, 2000).

The occurrence of the two above described mechanisms show the influence of bed temperature on the defluidisation time, and also on the structure and composition of agglomerates.

It is also quite probable that agglomerates are initiated from burning char particles (Lin et al., 1999). The particle temperatures may significantly affect the agglomeration temperature, and high temperature may be responsible for the release of “dangerous” compounds (Öhman, 1999). This may be the dominating way for potassium to be transferred to the sand surfaces. Bed temperature is, however, much easier to measure than particle temperature. Up to now, no mathematical correlation between agglomeration tendencies and fuel particle temperature has been developed.

Latva-Somppi (1998) reported that bed agglomeration of paper mill sludge occur in a pilot-scale BFB combustor only at a temperature higher than 1000 °C, suggesting that the refractory nature of the ash-forming constituents results in non-agglomerating bed behaviour.

As the formation of melted material plays a major role in the occurrence of bed agglomeration, prediction of the ash-melting behavior is considered essential. Both theoretical, experimental and laboratory methods, exist for this purpose – slagging and fouling indices based on the chemical composition of the ash; standard ash fusion tests (Jung et al, 1991); compression strength tests, (Skrifvars et al, 1998b); shrinkage measurements, high temperature microscopy, lab-scale combustion tests (Coda et al., 1999, Lin and Dam-Johansen, 1999, and Öhman, 1999)-.

Öhman has developed an elementary technique, "the controlled fluidized bed agglomeration test" (Öhman, 1999). Each experiment starts by "ashing" the fuel in the reactor (100 mm in diameter and 2000 mm in height). Fuel feeding is then stopped, and the bed temperature is increased by external heat. Combustion gases, from a propane burner, are continuously fed to the system to obtain a combustion atmosphere. The agglomeration temperature is then determined by monitoring temperatures and bed pressure. In this way, "intrinsic" properties of the fuel ash-forming constituents can be found out; one limit of the approach is, however, that the combustion environment is simulated and the real thermal histories of the fuel particles are therefore not taken into account.

Varying boiler operational parameters can successfully mitigate bed agglomeration phenomena. Early studies have indicated that larger particle size, lower temperature, higher fluidisation velocity, would decrease the tendency of the particles to agglomerate (Siegell, 1984; Wunkowski, 1989; Illy, 1991). If agglomeration tendencies occur, the bed material needs to be changed more frequently, causing an increment in the operational costs of the boiler.

When co-firing a biomass fuel with coal, its tendencies to agglomerate with the bed material may be mitigated, since the in-bed ash composition may be altered towards high melting temperatures. Lin et al. (1999) observed this phenomenon when co-firing coal and straw in a small-scale BFB reactor, but only at bed temperatures up to 800 °C. Control of in-bed agglomeration and significant reduction of agglomeration phenomena was obtained during industrial test runs by blending wood into rice straw (Salour et al, 1999), at bed temperatures lower than 800 °C.

Alumino-silicates minerals (which are usually present in the coals) may behave as sorbents for biomass-fuels like straw and bark, therefore mitigating bed agglomeration. Recent studies (Öhman et al, 2000) indicate that kaolin species may adsorb potassium-species in the bed, leading to increased bed agglomeration temperatures due to decreased melt fraction, i.e., depletion of potassium content in the coating. The mechanism proposed is involving reaction (3), as potassium-aluminium silicates have higher melting temperatures than alkali silicates.

Other studies indicate that clay additives are effective to reduce bed agglomeration tendencies when firing low-rank coals (Vuthaluru, et al, 1999). A positive impact of the ferric oxide used as bed material to replace silica sand was found (Grubor et al, 1995). Utilisation of bauxite had a positive impact on the bed agglomeration reduction when burning hazelnut shells (Vivarelli, 2000).

2.8 Fate of toxic trace metals upon fluidised bed combustion of biomass/waste

One reason for the recent widening of combustion research activities to the behaviour of the heavy metals has been the acknowledgement of the health risk associated to their toxicity, persistence and accumulation in the environment. Combustion processes involve significant risk of emitting pollutants to the environment, as many fuels usually contains heavy metals in trace concentrations², which have been identified as having adverse effects on human health and natural environment.

The healthy risk related to toxic metals is not only isolated to their release in the flue gas but also to the way they are associated to the fly ash (Lind, 1999).

Many wastes contain metal constituents, which, upon entering into a combustion environment, may be transformed into species or physical forms, and finally emitted. Metals with high vapor pressures at stack temperatures, like Hg and Se, may be emitted largely in vapor phase from the stack; other metals, with lower vapour pressure, may be emitted into the environment in form of enriched, tiny particles, (Clarke et al., 1992). Once emitted from the stack, metals in the gas phase or under particulate form are transported by the plume and dispersed into the atmosphere; during this process they can change their size and composition; the metals are then deposited back to the earth surface through wet and dry processes. Particles emitted by combustion sources are known to cause fibrosis, acute exacerbation of asthma and chronic obstructive pulmonary disease (Cenni, 2001). Carcinogenic effects are reported for As, Cd, and Ni and in special cases also for Cu, Fe, Co, Pb, Mn, and Zn; damages to the central nervous system and birth defects (Linak, 1993) due to the exposition to these toxic trace metals are well known.

Release of potentially toxic metals has recently received attention by regulatory authorities. The 1990 Clean Air Act Amendments, of the U.S. EPA, have targeted 11 elements (As, Be, Cd, Co, Cr, Hg, Ni, Mn, Pb, Sb, and Se) for potential control according to the “maximum achievable control technology”. Specific legislation and reductions are currently proposed in many countries (Smith et al., 2000).

² **Definition of trace metals and of heavy metals** Martel (1999) reports that in literature there is not a unique definition for heavy metals. The heavy metals are generally those metals with a density higher than 5 g/cm³ at 300K (chemical definition). With the progress in the metal toxicology, heavy metals are usually defined as those with toxic properties. Usually these metals are present in the fuels in trace concentrations, and this is why sometimes the two definitions are overlapping. In this thesis, we will typically speak about “toxic trace metals”. Cd, Cu, Cr, Ni, Mn, Pb, Zn (the elements under investigation in this work) belong in any case to the heavy metal group according to the classic chemical definition.

Fossil fuel combustion is the major source of emissions of Hg, Ni, Sn, and V in the environment, and the second large of Sb, Cd, Se and Tl (Clarke et al, 1992). While emissions from other sectors, such as municipal waste incineration, are currently being reduced, emissions from coal combustion are either remaining constant or not reduced at the same rate. This imposes the urgency of acquiring more detailed knowledge on the behaviour of trace metals upon coal firing and upon co-firing of coal and waste, and the necessity of determining possible measures to reduce their release in the atmosphere.

The toxicity of an element, and hence its environmental impact, is highly dependent on the formation of specific compounds (Lind et al, 1999). The main question is whether the metal will leave the combustor as vapour or as submicron particle, both difficult to isolate and collect from the air environment, or whether it will form or combine with collectable larger particles. Chemical reactions of an element with the ash may lead to the formation of chemically bound “benign” toxic compounds; on the contrary, surface condensation, in addition to the highly enriched fine particulate, usually creates particles with an easily leachable toxic surface coating. This enables the transport of the trace element into the surface, water, soil, and finally in the groundwater. (Valmari et al, 1999a, Lind, 1999; Meij et al, 1984

There is a vast literature and research concerning the origin and classification of trace metals in the coal. A summary of the mode of occurrence of the trace elements in coal is available (Clarke et al, 1992). For many trace elements the occurrence can be determined only speculatively, as most of the studies are based on indirect measurements, generally supported by leaching behaviour or density determination (Querol et al, 1995).

Finkelman (1999) lists its level-of-confidence about the modes of occurrence of many trace elements in the coal. (10 the highest level, 0 the lowest level). Mn is reported to be organically bounded or as carbonate (level 8); Pb as pyritic form (level 8); Cu as sulfides or organically associated (no level); Cd as clays or organically associated (level 8); Zn as ZnS or organically associated (no level). Linak et al. (1993) have proposed for coal an analogous classification of trace elements as reported for the main ash-forming constituents (included, excluded, and inherent). In wastes, speciation may be of different nature.

A fundamental overview concerning the behaviour of the trace metals upon combustion has been proposed by Linak et al (1993). **Figure 3** shows a general model of trace metal transformation paths.

The speciation of the trace metals in the fuels influences their behaviour upon combustion. In dependence on their mode to enter the combustor, metals may be either confined in the char matrix, or enter in the gas phase as char undergoes oxidation process, or released during devolatilisation phase.

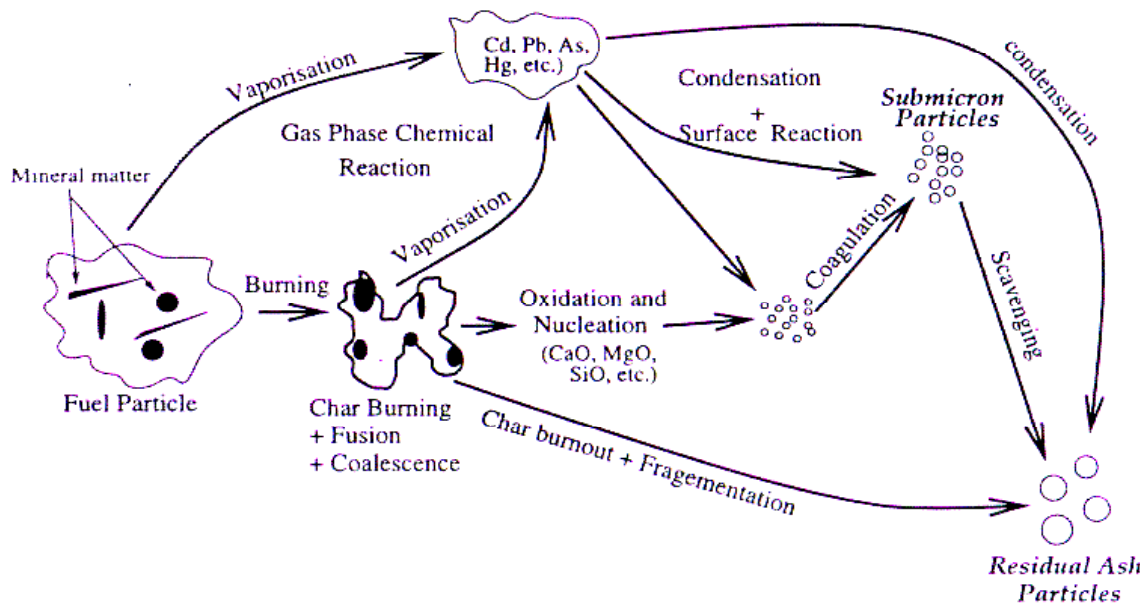


Figure 3: The fate of trace metals upon combustion (Linak et al, 1993).

The release of a metal into the gas phase into the combustor depends on:

- The form of the element when entering the combustor;
- Temperature;
- Gas composition (Linak, Wendt, 1993; Seeker, 1990). The vaporisation of some elements (e.g. Pb, Cd, Cu) may be influenced by Cl concentration in the gas (Verlhust, 1996). Chlorides of all metals have higher vapour pressures if compared to their correspondent oxides.

The metal may react with the included mineral matter structure (like silicates) to form stable compounds, which fail to vaporise. The metal, either in form of a vapour, or in solid phase, may undergo further transformation to other physical form, like being captured into the ash particles. Upon cooling, a metal vapour may condense on the surface of existing particles (heterogeneous condensation), including sorbents, or alternatively, nucleate homogeneously.

2.8.1 Enrichment on submicron particles

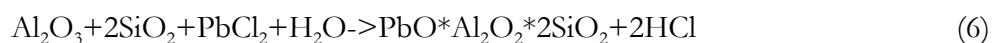
Many of the potential toxic trace metals are enriched in sub micrometer aerosol fraction of the flue gas (Meij, 1989, Linak et al, 1993). The high surface area of the sub micron particles relative to the residual ash particles results in the enrichment of a certain element on the sub micron particles (Senior et al, 2000), being associated to the vaporisation of these species, followed by their condensation on the surfaces of the pre-existing particles in the flue gas (Lind, 1999). In addition, the chemical reaction of trace element vapours on the fly ash particle surface would preferentially lead to their enrichment in the sub micron particles (Linak et al, 1993).

The time-temperature history of the combustion gases determines the condensation behaviour of the gaseous species. At 500 C aerosol nuclei tend to coagulate very quickly at small residence times (less than 0.1 sec), but at larger residence times (between 0.1 sec and 1000 sec) the coagulation rate slows considerably and the aerosol accumulate in a mode between 0.1 and 1.0 μm (Linak et al., 1993). This leads to the conclusion that other mechanisms than coagulation should be predominant in the formation of aerosol mass from sub micron fraction, as heterogeneous condensation.

2.8.2 Transformation paths upon FBC combustion

As previously discussed the ash formation under FBC conditions is strongly affected by the interactions of the fuel particles with the bed material. Upon FB combustion, a large surface area for the trace metal capture is provided by the bed particles, which may act as absorbents for gaseous-ash forming constituents. Collision of the fuel with the bed material and attrition phenomena may lead to the formation of fine fuel/char particles in the bed. Sintering of ash particles may initiate the occurrence of a molten phase. In the molten phase some trace metals could be captured, as their solubility in the melting phase could be high.

It has been recently shown that, under FBC conditions, some commercial sorbents may effectively scavenge a number of volatile metals. Kaolinite may be employed *in situ* as an additional bed material in the FB combustor, as it can effectively remove Pb according to a process of reactive adsorption, similar to what described for alkali chlorides, and occurring in presence of water vapor (Davis et al, 1999).



In a study showing the (according to the influence of dry sorbents injection on the formation of submicron particles at high combustion temperatures, Cd was also effectively captured by kaolin and bauxite (Uberoi et al., 1990a). The effectiveness of these sorbents for trace components must be however still proved. Addition of limestone to control emission of SO₂ in FBC conditions has been found to have negative effect of increasing trace element emissions: emissions of Pb, Cd and Mn were enhanced, and a corresponding increase in particulate emissions, which can be associated to an increase in fine particulate loading when limestone is added (CRE, 1987).³ However, it is difficult to establish whether a contribution comes from limestone or dolomite, which contain usually minor carbonate phases like MnCO₃ (rhodochrosite), or cerussite (PbCO₃) or smithsonite (ZnCO₃).

Most of the studies concerning toxic trace metal have dealt with coal combustion and with waste incineration (waste-to-energy systems). So far few works concerning the co-combustion have been performed. Only recently, investigations have been focused the fate of toxic trace metals on co-incineration of industrial waste and sewage sludge with coal, and RDF/Coal (Cenni et al, 1998; Reoper et al, 1999; Åmand et al, 2001). Main goal of these studies is to determine whether and how the co-firing of fuels with different combustion characteristics is going to affect the ash formation and the trace metals behaviour in the fluidised bed, and to assess the consequences in the post-combustion zone.

The fate of toxic trace metal upon biomass combustion has attracted recent interest, only partially associated to emissions but to the possibility that some of these toxic metals may accumulate in the ash streams, thus preventing the recirculation of the ash back to the soil.

Although the wood and straw have much lower trace metals concentrations than coal, the presence of a high organic substrate may alter the way these trace elements behave during gasification/combustion. Few data are known which compare the emissions of biomass like wood or straw versus coal under FBC conditions (Aho et al, 2001).

Few studies are known concerning the volatilisation of heavy metals during the fluidised bed combustion of biomass. Lind et al (1999a) have performed detailed aerosol measurements by means of low-pressure impactor (LPI) in a large-scale CFBC burning forest residue. Measurements were performed downstream the convective back pass and upstream at 830 °C. During combustion of forest residue, most of the trace elements studied (Cu, Zn, Cd, Pb) were found on the coarse fly ash particles and none of the elements were enriched in the fine particles at the inlet of the electrostatic precipitator. The gas-to-particle route for Cd, Pb, and Cu was

³ CRE, 1987, Trace element emissions from fluidised bed combustion Unit, Final Report, Technical Coral Research,

attributed to chemical surface reactions with silicates. Similar results were obtained during combustion of willow (Lind et al, 1999b). In this case, the retention of the toxic trace metals on the coarse fly ash particles has been attributed to their agglomeration from up to thousands submicron primary particles who prevented their condensation and subsequent enrichment in the fine particles.

2.8.3 Thermodynamic equilibrium studies

Equilibrium studies have proved to be of great value to understand the fundamental chemical paths affecting the distribution of the trace metals under combustion. Mojtahedi (1987) related for first the speciation of trace metals in coal combustion and gasification processes; work has been extended on biomass combustion (Nordin, Ljung). A fundamental work by Frandsen (1995) gives a complete overview of the equilibrium chemistry of the trace metals, though excluding the interactions with the ash matrix.

Several programs and databases have been developed by governmental institutions (NASA-CET89), universities (Eriksson et al.; Frandsen, 1995; Bale et al, 1995), and commercial companies (HSC, Roine A., 1997). Round robin tests for comparison and validation of the programs have been also performed (Frandsen et al. 1996).

Limitations to utilise the equilibrium studies are due to the fact that the effects of local heat and mass transfer related to physical changes of the fuel during heating up process, devolatilisation, and oxidation, are not taken into account. The initial metal speciation is not known. All the species that occur in the combustion system need to be taken into account; differences between thermodynamic packages may arise due to the presence or absence of some chemical species in the calculation database.

2.9 Paper sludge: behaviour of toxic trace metals upon combustion

The behaviour of toxic trace metals in sludges like denking and biological sludges, has been found to be strongly affected by metal interactions with the solid substrate (mostly with the Al/Si structure) which acted as a limit to their vaporisation.

Rink et al. (1995) observed that, during fluidised bed incineration of sludge from biological treatment, the ash was formed of loosely agglomerated particles and solid fused spheres. Cd and Pb encapsulation within a Si-Al-Ca based glassy structure was observed.

Kozinski et al. (1995) investigated the distribution of heavy metals inside the fly ash particles generated in a pilot-scale FBC reactor during combustion of denking sludge spiked with Pb, Cd, Cr and Ni nitrate solutions. Analysis of radial profiles inside the particle, performed on a

computer-controlled electron-probe microanalyzer (EPMA), indicating that these metal elements were generally located in regions near the particle's core, while the lighter metals were present across the entire cross-section of the particles. This behaviour has been attributed to the migration of some of the metal species inside the molten interior of the particles; the light metals may move only to locations closer to surface, left by species already vaporised, while heavy metals fragments may be less mobile. They also suggested that reactions between Pb and Si-Al-dominated compounds to form metal aluminosilicates could have occurred.

Holbert et al. (1998) investigated the trace metal behaviour upon the thermal treatment of a bio-sludge by means of bench-scale reactors (a muffle oven and a tube furnace reactor (TFR) assembly). Leachability tests were performed to provide insight of the extent of metal immobilisation in the ash. It was observed that Cd and Cr retention by ash was a strong function of the treatment temperature of reactor. Pb immobilization was seen to be due to structural changes as the temperature approaches the ash fusion point, in agreement with Kozinski's studies. It was also claimed that Pb might react with ash mineral phases to form lead silicate or lead alumino-silicates.

A similar finding was obtained by Latva-Somppi et al. (1994), who indicated that the ash-forming minerals in deinking sludge, such as clay, calcite, talc, do not release significant amount of trace elements into the gas phase upon FB combustion. The results reveal that trace elements did not migrate significantly in the ash structure, but that they may diffuse in the ash structure in case this is highly molten or sintered.

Ash from deinking combustion has been claimed to have sorbent properties for some toxic trace metals. The ash residue obtained after thermal treatment of the deinking sludge, is composed by a mixture of kaolin, calcium and trace quantities of metals like TiO_2 , Fe_2O_3 , MgO . Measurements performed by means of a 11-stage LPI, during experiments injecting the residue in an 18kW downflow furnace utilising aqueous metal salt solution, indicated the ability of the ash residue to capture Cd and Pb simultaneously (Davis et al., 1999).

Recent studies (Göttsching et al, 1996) have shown that heavy metals from paper fillers are insoluble in water, as they are fixed in the crystal structure, so that the contamination in water by heavy metals may result almost insignificant. Therefore, the reactivity (in terms of volatilisation under combustion conditions) of these components is not expected to be high.

All these studies show the importance of the metal-substrates interactions between trace metals and ash structure dominated by Al/Si compounds. The results have been generally obtained for deinking sludge, and need to be validated for other kind of recovered-paper treatment wastes.

2.10 Conclusions and work program of this thesis

With this literature review, an attempt has been made to cover the most important topics on ash behavior and ash-related problems for solid fuel FB combustion, giving emphasis on the differences between coal and biomass /waste combustion.

This thesis is motivated to by the need to obtain a more profound understanding of ash behaviour during paper sludge co-combustion. Deinking sludge combustion had been investigated in the past (Latva Somppi, 1998), but less work has been done on other types of paper recycling-derived waste streams. Utilisation of paper recycling-derived waste streams is of extreme economic interest to avoid the costs for landfilling disposal and to acquire a low-cost fuel. Motivation of acquiring knowledge is justified also by the fact that so many different “paper sludges” exist as many paper mill treatment plants.

Sludges are currently co-fired with other bio-waste fuels of the forest industry, (like wood waste or bark); however, its combustion behaviour upon co-firing with coal, or with other biomass fuels, like straw, has been practically never investigated on a fundamental level. The possible consequences in terms of ash handling are unknown, as well as the environmental impact associated to the fate of toxic trace metals.

The present study aims at characterising the combined combustion under FBC conditions of such fuels like coal, straw and paper sludge, characterised by different physical and chemical characteristics. To the author’s knowledge, this is the first study reporting extensive data on ash behaviour upon co-combustion of such fuel blends.

To understand where major change of the process characteristics with respect to combustion of single fuels may occur, several “steps” have been followed to conduct a complete characterization of the combustion behavior of the blends.

A detailed fuel characterisation has been performed on different types of paper sludges. This has been done to define the effects of the sludge characteristics on ash behaviour.

To gain knowledge of the influence of paper sludge mineral matter constituents, kaolin and calcite, on the CI behaviour, and on the enrichment of risk elements, additive-based test runs (with Kaolin and calcite) have been performed.

Combustion experiments of paper sludge as single fuel have been performed; the results have been compared to a typical deinking sludge. The experimental comparison has been done in order to estimate the differences occurring between the various sludges and the extension of the results to other waste streams.

The principal part of this thesis is based, however, on co-combustion experiments performed in

a 30 kWth FB test-scale combustor. Combustion test runs have been performed by blending paper sludge up to a share of 25 % in coal-based mixtures and coal/straw-based mixtures.

The aim of the experimental work was to obtain metal partitioning data for different blends under test conditions that simulate the time/temperature combustion and post-combustion conditions of commercial-scale boilers. Extensive mass balances and partitioning of all the principal ash-forming constituents in the different ash output streams have been performed, coupled with enhanced ash characterization. The study of the toxic trace metals has been restricted to the elements Cd, Cu, Zn, Pb, Mn, and partly to Cr and Ni. Preference has been given to these elements in view of their toxicity, and of their occurrence in high concentrations in the sludge.

The work has been mainly empirical. The empirical analysis has allowed, in first place, a qualitative observation of the mechanisms of ash formation, and the individuation of the occurrence of interactions between the inorganic matter components.

A fundamental part of the work is related to the comparison between the experimental data and the results of thermodynamic equilibrium calculations, providing the theoretical speciation of the elements in the fuel blends at combustion and post-combustion conditions. This comparison gave highly valuable information on the fate of the inorganic constituents, especially in relation to the occurrence of operational problems such as bed agglomeration; it allowed an estimation of the real risk associated to enrichment of toxic metals in the fine fly ash, too. The comparison has been of great advantage in order to gain insight on the governing mechanisms of the ash-related phenomena, and furthermore, has showed the limitations of the used investigation methodology, especially as far as the dependence on temperature concerns.

The thesis reports also a study on experimental results of a combustion test-campaign in a large-scale CFB boiler (80 MWth). The experimental campaign has been performed burning the same fuels as in the test-scale facility, and a qualitative comparison between the results of the two facilities has been made with respect to the ash behaviour. This comparison is closed by a critical evaluation regarding the scale-up methodology for FB boilers.

3. METHODS AND TOOLS

3.1 Experimental investigations: introduction

In this chapter an introduction will be given on the methods utilised in the study:

- the experimental methodology;
- the equilibrium calculation program used to determine the speciation and the melting behaviour of the ash components;
- the calculations concerning the mass balances on the overall ash and on each single element;
- the enrichment factors;

Mass balances are the basic tools to get information on the retention and partitioning of the elements at high-temperature and low-temperature locations in the combustion facility. They allow also a qualitative comparison with the results of the equilibrium calculations providing the speciation and phases of the elements over a large temperature range.

3.1.1 Description of the test-scale facility

Figure 1 shows the atmospheric fluidised bed combustion reactor used for the test runs. The test-scale facility (TSF), operating at IVD, has a max thermal input of 30 kWth. The facility is capable of firing a wide variety of fuels, and of reproducing the typical gas temperatures and compositions of the commercial FBC systems. The reactor consists of heat resistant steel tubes with an internal diameter of 108 mm in the bed region, 135 mm in the freeboard section and a total height of 3 meters. The operative parameters can be varied in the TSF independently on each other.

The reactor is electrically stabilised by means of electrical heating in five different zones, which can lead to wall temperatures up to 950 °C. Simultaneous use of electric heating and input energy from the fuels allow the reactor to run under constant conditions over a long duration time. The electric heating is used to start-up the reactor, and bed temperature is adjusted by means of the fuel dosage. The fuel is dosed by a screw feeder and is introduced at the bottom of the bed. In the case of a fuel blend, this is either dosed pre-blended, or the secondary fuel is supplied by an additional dosage system. Combustion air is introduced at the bottom of the combustor after passing through an electric heater. The primary airflow is usually heated up to a temperature

range 300-400 °C. By means of lateral openings, the possibility of secondary air supply for air staging is also provided. Ash particles are removed at the exit of the freeboard by means of a cyclone (stabilised at a temperature of 500°C), and of a ceramic candle filter (150 °C). Under BFB conditions, the typical fluidisation velocity is 0,6 m/s, corresponding to a mean residence time of 5 sec.

By means of an auxiliary return leg, the combustion reactor may also work under CFB conditions. In this case it operates at higher fluidisation velocities, in the range 1,2- 1,4 m/s, and with a corresponding residence time of about 3 sec. The return leg (diameter 100 mm) is also equipped with an electrical heating, which is usually kept at a temperature lower than the reactor, thus allowing a manual control of the temperature in the bed. Fluidisation air is injected at the bottom of the return leg; this is usually 1/10-1/15 of the total fluidisation air.

The facility is equipped with a data acquisition system, which records for each test run the gas composition at the stack, pressure drop in 5 locations (including 2 in bed and 1 in the freeboard), the gas temperatures (air-flow temperature after passing through the electric heating, 5 gas temperatures in the combustion reactor) and 5 wall temperatures.

3.1.2 Experimental procedure and sampling method

For each test run, fresh quartz sand bed was used ($\text{SiO}_2 > 97 \text{ wt}\%$). The bed material particle size range was 0.3-0.6 mm for BFBC conditions, and 0.06-0.2 mm for CFBC conditions. The use of a fresh bed allows the prevention of contamination from the previous test run, as this is

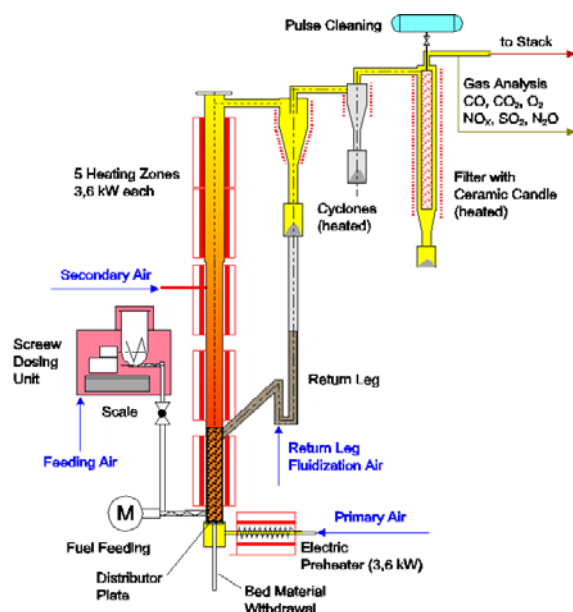


Figure 1: the FBC reactor at IVD- (here referred as TSF)

relevant to determine the amount and composition of the bottom bed ash. The easy replacement of the bed material represents one major advantage of providing reliable mass balances in a TSF rather than in a large-scale boiler.

The facility is firstly heated-up by means of the electric heating. Once that the fuel mass flow and the airflow have been adjusted, the combustion test run begins. The TSF reaches a stationary state in a relatively short time (max. 30 minutes), where the stationary time is related to the bed and freeboard temperature and O_2

concentration in the flue gas. The variation of the bed temperature was obtained by means of a variation of the fuel mass flow, while the electric heating was usually only used to start-up the facility.

Each test was characterised by a minimum duration time of 5 hours. The exact duration time has been set in dependence of the type and number of gaseous sampling. It was set that stability operative conditions were reached when a variable like gaseous HCl was stabilised. A typical trend for HCl is shown in **Figure 2**.

Attention was paid to the use of the pressured nitrogen flow cleaning system of cyclone and filter in order to avoid interference with gas sampling lines. The cleaning system has been put in operation when there was no connection with the wet-chemical equipment at the stack.

Table 1 and **Table 2** list all the main experiments performed in the study, indicating the variation of the most important operational parameters.

3.1.3 Mass flows and mass balances

At the end of each test run, the ash amounts from the **bottom** (bed for BFB conditions, bed and loop seal for CFB conditions), **cyclone**, and **filter**, were removed.

Performing ash and gas sampling during the test runs allowed the determination of mass balances, to estimate the retention of the total fuel blend-ashes in the different output streams. Under the hypothesis of neglecting the ash release in the gas phase to the stack¹, the ash-forming

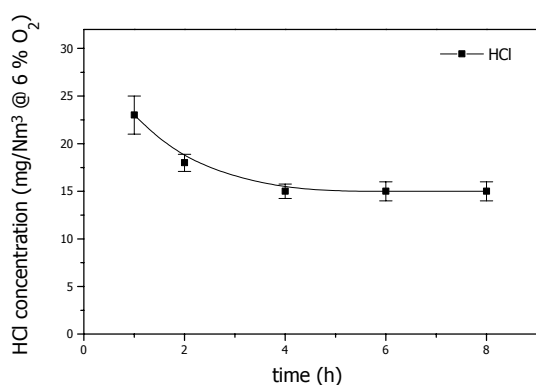


Figure 2 : The variation of HCl concentration sampled at different experimental duration times

constituents fed into the reactor either end up in the **bottom ash**, or as fly ash collected both into the cyclone (**coarse fly ash**)- and into a filter (**fine fly ash**). Measurements for S, Cl and trace metals at the stack were performed; thus information on their share in the flue gas was obtained.

The ash fractions can be calculated as quotients of the amount of element X removed with an ash-output stream and related either to the total output of X (bottom ash + cyclone ash + filter ash), or related to the total mass input fed into the reactor with the fuel

¹ The ash particles concentrations after the stack were measured according to standard wet-chemical methods (reported in Appendix II). They can be considered negligible in comparison to fractions recovered in the other ash streams.

blends. On the theoretical case of no mass loss during the test runs, and of neglecting the fraction of volatilized ash at the stack, the recovered ash mass should be equal to 100% of the fuel blend input: the two ratios should therefore be equivalent. A comparison of calculated ash fraction according to both methods was performed and the accuracy of the experimental methods allowed a total output for overall ash (as bottom + cyclone + filter) between 92 and 95 % of the total ash fed as an input with the fuel.

Ash was accumulating at the bottom either as single, residual ash particles, or in form of a coating on the bed material. To distinguish between the two fractions, part of the spent bed material was sieved, to obtain a particle fraction corresponding to the original bed material size.

3.2 Equilibrium analysis: introduction

The fundamental chemistry of the main ash-forming constituents and trace elements of the fuel blends was investigated also from a theoretical point of view. The behavior of inorganic matter at different temperatures was studied utilizing an equilibrium model that minimizes Gibbs free energy of the system. A computer program "ChemSage" (Eriksson and Hack, 1990) was used together with selected thermochemical constants from the literature and electronic databases (Ebbinghaus, 1993; SGTE, 1996; Bale and Pelton, 1999). The equilibrium model that is described below was originally developed for describing trace element behavior in a bubbling fluidized bed facility burning biomass mixtures (Sandelin et al., 2000). The main part of the data was taken from the FACT, 1999 database (Bale and Pelton, 1999).

The method has been developed at the Combustion Research Group at Åbo Akademi University, Finland, where the calculations for the fuel blends of interest have been performed, too.

The model is described in details in many referred publications (Coda et al, 2001; Sandelin et al, 2001; Sandelin et al, 2000; Sandelin, 1999), including the number of species and solutions used and the assumption of the calculation methods.

Fuel	Operative mode	Air staging/total air ratio	Bed temperature (°C)	Additive dosage ²		
Paper sludge (ps 100)	BFB	0/1,6	800	-		
			850			
			880			
		0 /1,6	850	Kaolin		0.25
						0.4
						0.6
				Bauxite		0.4
				Limestone		0.4
						0.6
		0 /1,4	850	-		
0/1,2	850					-
0,8/1,2	850					
Deinking sludge	BFB	0/1,2	850			
		0/1,4	800			
			850			
			880			

Table 1: List of the major operative conditions for the test runs in the TSF-combustion of single fuels

² Dosage is defined as the ratio between the mass flow of additive and mass flow of fuel ash

Blend				Operative mode	Air staging/total air ratio	Bed temperature (°C)	Additive dosage ³	
Coal	Straw	Paper sludge	Name of the blend ⁴					
100	0	0	c	BFB	0/1,4	800		
						850		
						880		
					0/1,2	850		
					0,6/1,4	880		
50	50	0	cs		BFB	0/1,4	800	
				850				
				880				
				920				
50	50		cs		0/1,2	850		
45	50	5	Csps5		0/1,4	880		
30	50	10	Csps10		0/1,4	880		
0	50	20	Csps20		0/1,4	880		
0	50	50	Sps50		0/1,4	830		
50	50	0	0% PS	CFB	0/1,4	810	Limestone, Ca/S = 2	
						870		
40	50	10	10% PS		CFB	0/1,4	810	Limestone, Ca/S = 2
							870	
35	50	15	15% PS		CFB	0/1,4	810	Limestone, Ca/S = 2
							870	
30	50	20	20% PS	CFB	0/1,6	810	Limestone, Ca/S = 2	
						870		
25	50	25	25% PS	CFB	0/1,6	810	Limestone, Ca/S = 2	
						870		
100	0	0	0% PS	CFB	0/1,4	810	Limestone, Ca/S = 2	
						870		
90	0	10	10% PS		CFB	0/1,4	810	Limestone, Ca/S = 2
							870	
85	0	15	15% PS		CFB	0/1,4	810	Limestone, Ca/S = 2
							870	
80	0	20	20% PS	CFB	0/1,6	810	Limestone, Ca/S = 2	
						870		
75	0	25	25% PS	CFB	0/1,6	810	Limestone, Ca/S = 2	
						870		

Table 2: list of the major operative conditions during the test runs in the TSF – combustion of fuel blends

³ Dosage is defined as the ratio between the mass flow of additive and mass flow of fuel ash

⁴ The name of the blend will be reported in the corresponding figures in the next chapters

3.2.1 Comparative approach: equilibrium calculations vs. experimental ash partitioning

In a global equilibrium analysis, imaginary reactants are introduced to the hypothetical equilibrium reactor (**Figure 3**) and the most stable state of the system is theoretically determined by minimizing the Gibbs free energy of the system that is independent of time. The amount of the elements included in the fuel and air is introduced into an equilibrium reactor and is equilibrated at a given temperature and pressure. The result of a calculation of this kind is the composition of the gas- and the condensed phases.

In the calculations, the main ash forming constituents and the trace elements were simultaneously included. The outcome of the equilibrium calculations method, as it was used in this work, consists of the elements speciation, (in terms of amount and composition) and their

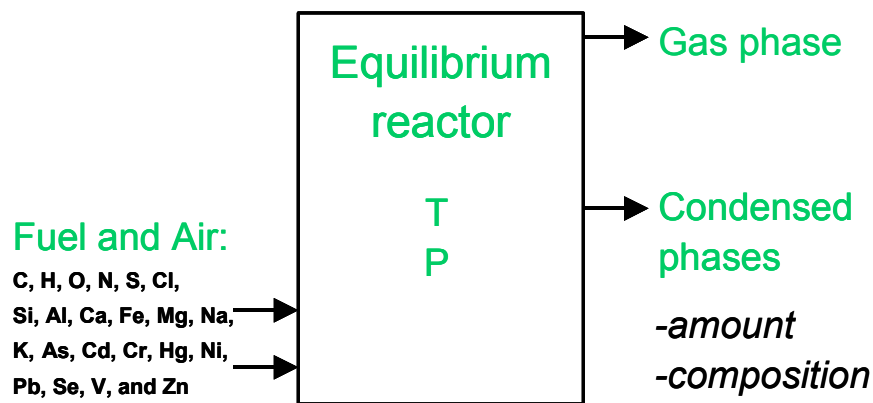


Figure 3: the schema of the equilibrium reactor (Sandelin, 2000b)

variation over a wide temperature range, usually 1200°C- 400°C⁵. In this way, the equilibrium analysis gives several “instantaneous pictures” of the chemical processes occurring in the combustor and along the flue gas-cooling path, thus helping to understand the fate of the different elements. **Figure 4** shows the „equilibrium reactors“, which repeats the methodology above described for three different temperatures, simulating the flue gas path at the TSF. This set of reactors was chosen to ensure compatibility with the experimental results. The experimental partitioning, based on ash samplings and flue gas samplings, furnishes direct information on the retention of the inorganic elements from high-temperature to low-temperatures locations (the bed- bottom ash-880 ° C; cyclone- coarse fly ash-500°C; candle filter- fine fly ash- 150°C).

⁵ At low temperatures (from 400°C) it is suggested that chemical reactions are “frozen” and only gas condensation phenomena occur.

Attention must be put on the fact that a combustion plant is not a system in equilibrium.⁶ Even if local and time-dependent conditions are not taken into account in the equilibrium description, the prediction of the equilibrium chemistry gives an overall picture of the chemical behaviour of the elements. It helps in understanding the factors affecting the speciation of the stable chemical species, and consequently, the reason for the elements partitioning.

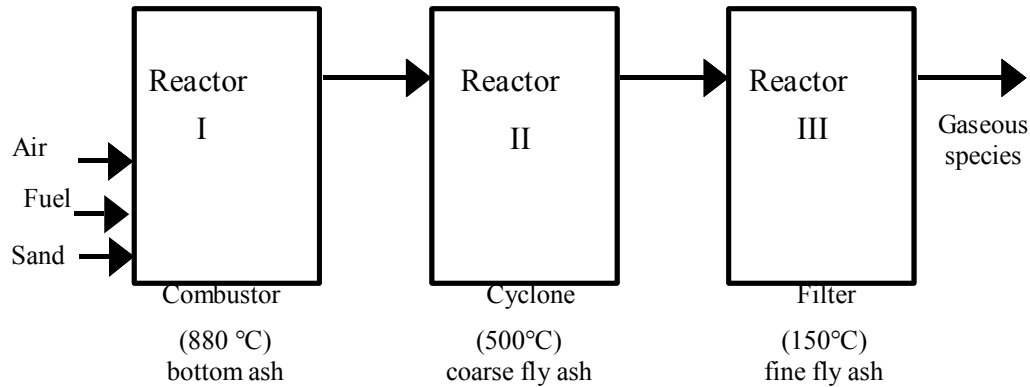


Figure 4: The “equilibrium reactors”

3.3 Definitions: mass balances-recovery rates- enrichment factors

The amount of element i removed with an ash-output stream is related to the total input of i in the fuel blend. The **recovery rate** is defined as follows:

$$RR_i = \frac{m_{bottash, i} \cdot c_{bottash, i} + m_{filtash, i} \cdot c_{filtash, i} + m_{cycash, i} \cdot c_{cycash, i}}{m_{fuel} \cdot c_{fuel, i}} \cdot 100 \quad (1)$$

Where:

$m_{bottash, i}$ = ash output mass flow (dry basis) of the bottom ash stream (Kg/h)

$m_{filtash, i}$ = ash output stream (dry basis) of the filter ash stream (Kg/h)

$m_{cycash, i}$ = ash output stream (dry basis) of the cyclone ash stream (Kg/h)

$m_{filtash, i}$, $m_{cycash, i}$, $m_{bottash, i}$ are calculated as mean value for all the duration time of the experiment once that, at the end of the test run, bed ash, cyclone ash, filter ash are collected and weighed. The bottom ash is composed by original bed material –sand- plus the ash, which remained in the

⁶ According to the simple methodology used, that associates the speciation of the elements over a certain temperature range with the partitioning of the elements collected in the material output streams, a CFB system is “less in equilibrium” than the corresponding BFB system. The gas/particle temperature-time history in a CFB systems is much more complex than in the BFB, due to the recirculation of the bed material flow in the return leg, and in the loop seal, usually at lower temperature (700 °C) than in the combustion riser. The mean gas residence time in a CFB combustor is also shorter than in a BFB combustor. Therefore, it can be expected that BFB systems are closer to equilibrium conditions than CFB ones.

bed during the test run. The original weight of the bed material must be subtracted to obtain the bottom ash, m_{bottash} .

$c_{\text{fuel},i}$; $c_{\text{bottash},i}$; $c_{\text{filtash},i}$; $c_{\text{cycash},i}$ = concentration of the element i in the fuel and in the ash output streams (mg/kg; dry basis).

m_{fuel} = it is defined as follows (Kg/h):

$$m_{\text{fuel}} = \frac{\int_0^{t^*} M(t) dt}{\int_0^{t^*} dt} \quad (2)$$

$M(t)$ = instantaneous mass flow as recorded by the data acquisition system (kg/h)

t^* = duration time of the experimental run (h).

The definition given above is valid only when firing a single fuel. Most of the experiments of the thesis concern fuel blends, so that the input mass flow of an element has to be calculated from the total contribution of the single fuels that compose the blend according to the blend share ratios.

$$RR_i = \frac{m_{\text{bottash},i} \cdot c_{\text{bottash},i} + m_{\text{filtash},i} \cdot c_{\text{filtash},i} + m_{\text{cycash},i} \cdot c_{\text{cycash},i}}{m_{\text{fuel}} \cdot \sum_{j=1}^3 c_{\text{fuel},j,i} \cdot X_{\text{fuel},j}} \cdot 100 \quad (3)$$

$c_{\text{fuel},j,i}$ = the concentration of the element i in the fuel j of the fuel blend (mg/kg)

$X_{\text{fuel},j}$ = the mass share of the fuel j in the fuel blend once that its share of the total energy input ($X_{\text{enb},j}$) is chosen. $X_{\text{fuel},j}$ (%) represents the mass of the fuel j which provides a fraction $X_{\text{enb},j}$ (%) of the total energetic input referred to coal (the main fuel in the blend)

$$X_{\text{fuel},j} = \frac{M_{\text{coal}} \cdot Hu_{\text{coal}} \cdot X_{\text{enb},j}}{Hu_j} \quad (4)$$

Hu_j , Hu_{coal} = low calorific value of the auxiliary fuel j and of coal (MJ/kg).

m_{fuel} in equation (3) is referred to the total mass flow fuel blend.

The portion of the element i recovered in each single ash-output stream k (k = bottom, filter, cyclone) can be therefore determined:

$$RR_{i,k} = \frac{m_{k,i} \cdot c_{k,i}}{m_{\text{fuel}} \cdot \sum_{j=1}^3 c_{\text{fuel},j,i} \cdot X_{\text{fuel},j}} \cdot 100 \quad (5)$$

The total ash recovery rate is defined as follows:

$$RR_{,ash,k} = \frac{m_k \cdot ash_k}{m_{fuel} \cdot \sum_{j=1}^3 ash_j \cdot X_{fuel_j}} \cdot 100 \quad (6)$$

ash_k ($k = \text{bottom, filter, cyclone}$) is related to the ash content of the k -ash output stream, and ash_j the ash content of the fuel j .

The recovery of the element measured as a vaporised fraction in the flue gas has been calculated⁷:

$$VR_i = \frac{C_{gas,i} \cdot V_{gas}}{m_{fuel} \cdot \sum_{j=1}^3 c_{fuel_j,i} \cdot X_{fuel_j}} \cdot 100\% \quad (7)$$

With

$C_{gas,i}$ = concentration of the element i in the dry gas (mg/Nm³, dry basis)

V_{gas} = flue gas volume (dry basis) (Nm³/h) determined from theoretical combustion calculations as volume of the combustion products (NO, SO₂, CO₂, H₂O) once that the elemental composition of the fuel blend and the m_{fuel} input are known.

The **enrichment factor** of the element i in the ash fraction k ($k = \text{bottom, filter, cyclone}$) describes the enrichment or depletion of the element i in the single ash fraction k versus its concentration in the fuel (fuel blend). (Meij, 1989)

$$ER_{i,k} = \frac{c_{i,k} \cdot \sum_{j=1}^3 X_{fuel_j} \cdot ash_j}{\sum_{j=1}^3 c_{fuel_j,i} \cdot X_{fuel_j}} \quad (8)$$

ash_j = the ash share of the fuel j . A value > 1 defines an enrichment of the element in the ash stream of interest, < 1 a depletion.

Enrichment factors may be used (Meij, 1989) to extract rapidly information concerning the propensity of the toxic element to be enriched on a certain ash fraction.

Although enrichment factors have been widely used in the scientific literature, much criticism has been put in this definition; a partial error may be introduced, as the total amount of the ash output streams may strongly differ from the mean ash content of the fuel blend (as some

⁷ When flue gas measurements have been performed, for some elements the total recovery rate has been displayed as sum of the recovery rate in each ash-output stream (RR_i) and the vaporised fraction in the flue gas (VR_i)

components may volatilise). The definition of the enrichment factor does not take this difference into account.

Therefore, a second enrichment factor has been introduced, which can be useful especially to study the propensity of the toxic element to be enriched on the small, fine particle ash in the flue gas, which are the most harmful. It relates the enrichment of an element in the coarse fly ash to the enrichment in the fine fly ash.

$$ER_{i,cyc/fil} = \frac{ER_{i,cyc}}{ER_{i,fil}} \quad (9)$$

3.4 Discussion of the methods

BFB combustors and, even to a higher extent, CFB combustors, are complex systems. Large uncertainties exist on the transferability of results from a small-scale facility to a large-scale combustor as far as ash behavior concern. This would in fact require not only knowledge of the bed hydrodynamics, but also of particle-particle interactions, of fuel combustion behaviour, and also of aerosol transformation processes. The simple mechanistic model on ash formation for CFB combustors for coal and biomass proposed by Lind (Lind, 1999) emphasizes that still more fundamental work is required before a complete mechanistic model on ash behavior for FB boilers can be reached. The reliability of scaling-up is associated, among the others, to the limited description of the interaction fuel-bed material.

If limitations exist in scaling-up the results obtained in test-scale combustion reactors to large boilers, on the other hand, full-scale experiments suffer from lack of constant operative conditions over the long term, and of precise experimental operational parameters. This occurs to a great extent for co-combustion conditions, as the number of variables to control is higher than upon combustion of a single fuel.

In this respect small-scale combustors take advantage of the possibility to supply useful information on the phenomena affecting ash formation and on the behavior of the major ash constituents and toxic trace metals.

The approach followed in this thesis is mostly experimental. With respect to the toxic trace metals, the study has focused on the emissions to the stack; a detailed characterisation of the particulate emissions and composition is not included. The formation of fine particles, on one side might improve the recovery in solid phase of the metals due to a high surface for reaction or condensation, but on the other side it could worsen the emissions of fine particulate escaping the filter.

The analysis of the risk associated to the toxic trace metals is based on a two-sized ash classification, one coarse (app. 100-20 μm), and one fine (10-1 μm) mode. This gives a fast response to the question, whether there is risk for a metal to condense on the finer particles or whether the metal will be primarily captured in the coarse particle size, meaning at high temperature locations in the boiler, thus minimizing the risk associated to their release into the environment.

4. COMPARISON OF ASH BEHAVIOUR: PAPER SLUDGE AND DEINKING SLUDGE

In this chapter a characterisation of the ash behaviour upon combustion of paper sludge and deinking sludge has been performed. A comparison has been built-up, based on experiments performed in the TSF operating under bubbling fluidised mode.

The aim of this investigation is twofold: firstly, to characterise the ash behaviour upon combustion of paper sludge, and, secondly, to obtain information on whether and to which extent paper sludge behaviour resembles deinking sludge, a fuel which has been previously investigated. In this way, knowledge can be obtained on the differences between the various waste streams from paper mill. This information will turn later helpful to characterise the behaviour of paper mill sludges upon co-firing with coal and coal/straw blends.

The paper sludge came from a paper mill in Grenå, Denmark, situated nearby a power plant. It is a mixture of sludge coming from primary treatment plants, where the coarse particles are

removed from the waste water, and of rejects of recovered paper. Deinking sludge was produced in a German paper mill.

4.1 Fuel composition

Analysis of the fuels used is shown in **Table 1**. Paper sludge has been partly dewatered to get it better fed in the furnace. The original moisture content of the paper sludge was about 25% wt.

Paper sludge contains much more chlorine in comparison to the deinking samples. This can be associated to the presence of plastic compounds. Due to the presence of extraneous material, (plastic, bottles cups, textiles, etc), paper sludge was highly inhomogeneous; the inhomogeneity was reflected to a high extent in the chlorine content of the samples. Chlorine was not homogeneously distributed in the fuel, as analysis from different samples show it was in the range 0,01-1,3 wt %.

Fuel	Deinking sludge (wt %)	Paper sludge (wt %)
Moisture	44,0	8,5
Ash (db)	40,0	3,9
C (db)	32,8	45,2
H (db)	4,7	6,3
N (db)	0,26	0,11
S (db)	0,1	0,07
O (diff) (db)	21,9	44,42
LHV (MJ kg ⁻¹)	12,3	19,1
Ash forming elements	(%ash)	(%ash)
K ₂ O	0,3	1,25
CaO	35,1	17,17
MgO	5,9	4,55
Na ₂ O	0,2	4,79
Al ₂ O ₃	9,9	6,1
SiO ₂	29,4	35,57
Fe ₂ O ₃	1,0	1,56
Cl	0,06	0,32
Trace elements	mg/kg	mg/kg
Hg	<0,06	0,06
Mn	45,5	10
Pb	42,98	15
Cd	0,4	0,07
Cu	192	20
As	2	0,5
Ni	41,7	10
Cr	77,23	14
Zn	141	150
Particle size (mm)	3-9	3-9

Table 1: Fuel and ash analysis of the sludges used during the combustion tests.

One relevant difference is the ash content of the fuels. Despite the presence of extraneous material, which accounts for approximately 5% of the total fuel mass, paper sludge contains much less ash than the deinking sludge. The ash analysis shows a predominance of kaolinite and calcite. Deinking sludge appeared as a much more homogeneous fuel.

The trace metal content of deinking sludge is generally higher than of the paper sludge. Hg content in the sludge is very low; the concentration is of the same order as in bituminous coal, but typically much less than a municipal solid waste. Cu and Zn are the elements with the highest concentrations in the sludge and, together with Mn, are classified as elements of potential high toxicity.

4.2 Mass balances and ash partitioning

The total partitioning for paper sludge ash is shown in **Figure 1**. Overall partitioning show that the inorganic matter of paper sludge is recovered to a 10% in the bottom bed ash, while to a larger extent it is recovered as coarse fly ash particles in the cyclone. 10% of the total inorganic matter is forming fine fly ash particles, recovered in the filter. This partitioning is typical of a large-scale BFB boiler, and therefore assures a good scale-up.¹

Figure 2 shows the total ash partitioning for deinking sludge. Unlike paper sludge combustion, the ash fraction recovered in the bottom bed ash when firing deinking sludge is about 70%, while only 18% of the total inorganic fuel fraction is recovered as coarse fly ash particles and (12%) as fine fly ash particles. Compared to paper sludge or paper rejects, deinking sludge is usually a higher-density fuel, and its ash content is also higher. The large particles size is

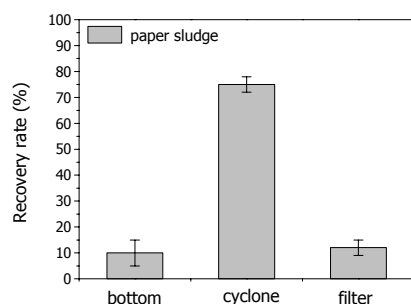


Figure 1: Total ash partitioning for paper sludge

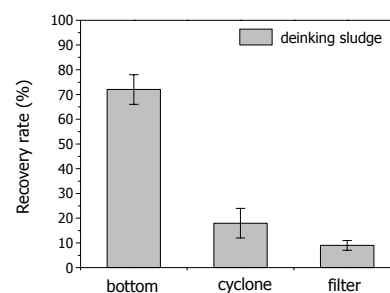


Figure 2: Total ash partitioning for deinking sludge

¹ It was observed that the variation of operative parameters like bed temperature and does not markedly affect macroscopic variables like ash composition and ash streams partitioning. The same behaviour was observed when varying the air ratio. This behaviour was similar for all the fuel blends under investigation

associated to specific deinking sludge characteristics (Latva Somppi et al, 1994; Latva Somppi, 1998).

4.2.1 Bottom ash and bed agglomeration

The partitioning of inorganic elements upon paper sludge combustion is shown in **Figure 3**. When firing paper sludge as a single fuel, the mineral matter constituents formed a coating upon the bed material, depositing on the sand particles surface. Negligible occurrence of single, isolated ash particles in the bottom ash was observed. Therefore the bottom ash corresponds totally 100% to the coating amount on the bed material. This phenomenon may be associated to the extremely high reactivity of the porous paper sludge particles, and to the fine particle size range of the inorganic components in the paper. The mean particle size range for paper coating and fillers is respectively, 0,2-2 μm and 0,2-20 μm (Latva-Somppi, 1998). Paper sludge burned mostly on the bed surface and, due to its porous structure, it could easily exchange its mineral

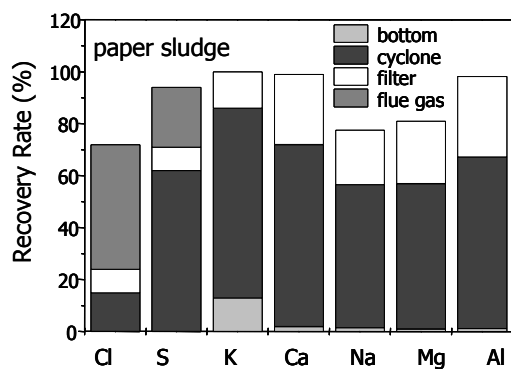


Figure 3: Element partitioning for paper sludge

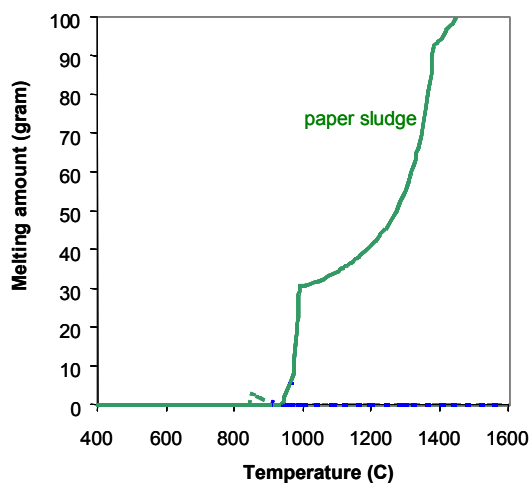


Figure 4: Melting of ash for the system paper sludge+ bed material

matter with the bed particles. The elements mostly enriched in the coating are K, and Ca. Na is found only at small concentration in the bottoms, and Al, Fe, Mg, are found up to few percentages of their correspondent fuel input. On the contrary, Cl and S are totally depleted in the bed, meaning that they are volatilised at bed temperatures.

Changes in the operative conditions of the reactor did not markedly affect the composition of the coating. No signs of bed agglomeration tendencies were noticed upon combustion of paper sludge at different load conditions.

Figure 4 shows the results of the equilibrium calculations reporting the melting behaviour of paper sludge: a system of air-fuel-bed material has been simulated, comprising 1,2 kg of paper sludge, bed material for one-hour

operation, i.e., approximately 34 MJ of fuel and 1.75 kg of bed material and air. This calculation allows to obtain useful indications on the possible occurrence of bed agglomeration phenomena. The picture shows that a liquid slag starts to form at around 940°C with the bed material. However, another melt, a liquid salt, is formed at temperatures between 840°C and 910°C, but its share is almost negligible. The liquid comprises mostly for Ca-Si structures. The main species are complex phases of Na-Ca-Si and Mg-Ca-Si based compounds.

Equilibrium predictions, showing the negligible presence of molten phases at typical bed temperature, are in good agreement with experimental results showing no signs of bed agglomeration.

Upon combustion of deinking sludge, bottom ash was composed mostly by heavy, single ash

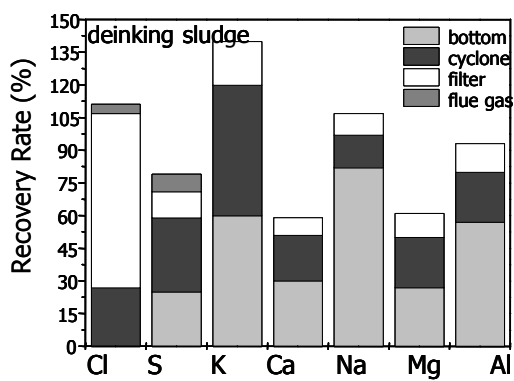


Figure 5 :Element partitioning for deinking sludge

particles, while a minor part, comprising for approximately 10% of the bottom ash, was forming a coating on the surface of the sand material.

The inorganic elements partitioning for deinking sludge is shown in **Figure 5**. Cl is totally depleted from the bed. The partial recovery of sulfur and Ca may be associated to the formation of CaSO_4 at bed temperatures. K, Na and Al are also

largely recovered in the bottom bed ash. For Ca and Mg a lower recovery in comparison to the total ash partitioning is observed. The coating composition, here not reported, is enriched on Al and K.

Upon combustion of deinking sludge, the ash accumulated in the bottom bed until the bed defluidisation eventually occurred. It is suggested that the ash accumulation signed the beginning of the defluidisation mechanism, rather than the melting of an ash layer coating on the sand surface. Visual observation of the bed showed that sintering of porous ash particles occurred, causing bed agglomeration; the coated sand particles participated only occasionally to the agglomerate ash growth. Intermediate sampling performed at different time intervals during the test runs indicated that the ash fraction in the bed was steadily growing, and that defluidisation occurred a gradual phenomenon, rather than an instantaneous one.

Large, porous ash particles formed agglomerates, which behaved in the bed as loose, jetsam agglomerates which segregated in the bed until defluidisation occurred. This phenomenon is in agreement with what observed by Lin et al. (1997). The particle size grew much larger than the

bed sand, up to 1-2 centimetres. Ca, Al, K, were found at high concentrations in the ash agglomerates. At typical bed temperatures, the sintering of this ternary melt can occur, depending on the composition of the mixture (Öhman et al, 2001).

Agglomeration tendencies of deinking sludge may be much improved in a large-scale unit, where higher air flow rates are used, as this helps keeping the larger particles under fluidisation; attention is required, as the bed material needs to be often changed to avoid operational risks.

Furthermore, in industrial units, the increase in bed static pressure may lead to a increase in bed particle fragmentation, thus additionally reducing the risk associated to agglomerate growth.

4.3 Fly ash formation and composition

Upon paper sludge combustion, 23 % of the fuel sulphur was detected in the flue gas as SO₂. The remaining sulphur is recovered mostly in the coarse fly ash. The fraction of Cl recovered in the ash is about 26 %; more than 65% of the total Cl is detected as HCl in the flue gas. The highest fraction of alkali is recovered in the coarse ash fraction: K and Na are recovered, respectively, to a share of 70% and 63%. Ca is recovered at about 80% in the coarse fly ash. Ca and Al, are however enriched also in the fine fly ash fraction.

According to equilibrium calculations, for the paper sludge system, sulfur exists under gas phase up to temperature of 920 °C, when a solid solution comprising alkali sulfates is entering the melt. K- and Na- sulfates phases begin to condense at furnace temperatures (850 °C); CaSO₄ is also formed at those temperatures. At about 800 °C the formation of sulfur-condensed phases is completed and sulfur is theoretically all retained under condensed phases. The equilibrium calculations are consistent with the experimental results, showing that a high share of sulfur is retained in the coarse fly ash.

As far as Cl is concerned, HCl(g) comprises along the temperature range 1000-400 °C for most of the Cl present in the fuel; KCl(g) and NaCl(g) exists at furnace temperatures in minor shares; at 800-850 °C the sulfation reactions are completed, and only a minor fraction of HCl is condensing at low temperatures (app. 500 °C) to form alkali-chlorides (Sandelin, 2000b).

The equilibrium calculations for Cl are consistent with the ash partitioning data, reporting that a high share of Cl exits under gaseous phases at filter temperatures (150°C), while only a minor fraction is condensing.

The results of leaching analysis performed on fly ash samples for paper sludge combustion show that a high share of the alkali (up to 70% in the fine fly ash) is bounded as water-soluble compounds (presumably sulfates or chlorides). The molar ratio $(K+Na+2Ca)/(Cl+S)$ assumes

values very close to 1, for both fine and coarse fly ash modes, indicating that for paper sludge Cl and S are only bounded in form of leachable form of alkali-sulphates or alkali chlorides.

As far as deinking sludge concerns, the results show that Cl is enriched in the fine fly ash rather than in the coarse fly ash. For sulfur, on reverse, there is an equal partitioning among the various ash streams. The behaviour of Al is very similar. K is also highly recovered in the cyclone; Na, on the contrary, is highly recovered in the bottom ash. Mg and Ca are relatively more enriched in the coarse fly ash fraction rather than in the fine fly ash fraction.

To conclude, for paper sludge combustion, most of Cl is measured under gaseous form as HCl, and only a minor share is retained as alkali chlorides in the fly ash; for deinking sludge, a large share Cl is recovered in the coarse and fine fly ash, however, being its content much lower than in paper sludge, lower risk associated to corrosion due to alkali chlorides deposition is expected. For paper sludge, the formation of alkali sulfates and of CaSO_4 has been observed by comparison of XRD analysis, ash partitioning, indirectly, by leaching analysis, and confirmed by equilibrium calculations. Sulfur-self capture has been observed also for deinking sludge. The partial recovery of sulfur in the bottom ash for deinking sludge is associated to the retention of CaSO_4 in the bottom bed.

4.4 Ash particles structure and distribution

XRD analysis, effected on a sample of paper sludge coarse fly ash, showed high detection of the following phases: K_2SO_4 ; CaSO_4 (anhydrite); sanidine - KAlSi_3O_8 -; albite - $\text{NaAlSi}_3\text{O}_8$ -, KCl.

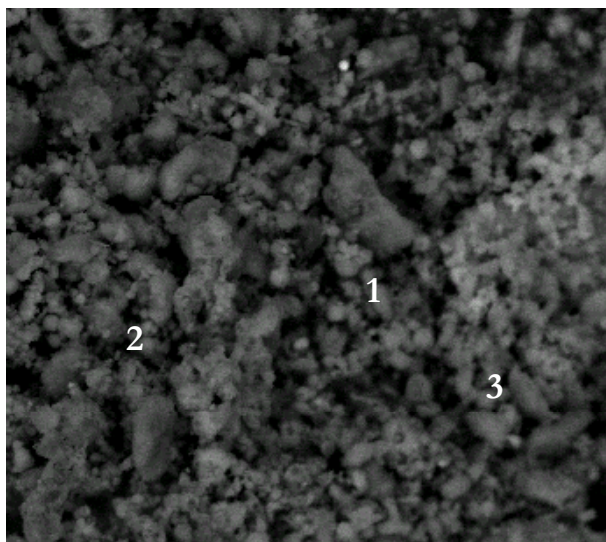


Figure 6: SEM picture of a sample of paper sludge fly ash -300*SE magnification

Phases detected to a less extent were: Na_2SO_4 ; complexes of calcium-sulfates-silicates; calcium silicates.

The SEM image in **Figure 6** shows the uniform presence of porous ash structure. Only a very few compact, larger smoother particles, can be observed. Agglomerates size was less than few micron, as probably the size of the original coating/fillers of the paper mineral matter. On points 1 and 3, high Ca concentrations have been recognized, associated to Si-Al, suggesting

the occurrence of Ca-Al-silicates; the system K/Cl is also slightly detected. On points 2 and 4, on the smoother surfaces, Si is highly detected, which would indicate the formation of SiO₂ or, associated to K and Al-also detected-, the formation of K-Al-silicates. Smooth particles may derive also from sand fragments.

It is suggested that the mineral particles in the paper sludge have melted or fused during combustion, forming agglomerates of fine ash particles, creating unregularly- shaped structures, with a final particle size in the range 8-10 µm. When the particles burn, the mineral matter in the sludge may partly melt, forming sintered and porous particles that agglomerate and create structures larger than the original mineral matter constituents, resulting in a skeleton-type ash structure. Upon firing deinking sludge, the formation of sintered, porous ash particles had been observed (Latva-Somppi, 1998), and in the case of paper sludge a similar phenomenon may occur.

According to qualitative estimations, particles around 10 µm with composition of Ca-Al-Si systems might partly melt at temperatures around 1100 °C, getting sticky and initiating the fly ash agglomeration process (Latva-Somppi, 1998). As it will be reported more extensively in the next chapter, the temperatures of burning char particles from paper sludge are very difficult to estimate; however, the peak temperatures may exceed the bed temperatures up to several hundreds degrees and may be sufficient for a partial particle fusion.

The formation of the porous ash is likely to have effect on the capture and condensation of other trace metals or generally gaseous species, as it will be discussed later on. ²

Upon combustion of paper sludge, the mean particle size for the coarse fly ash fraction is $d_{50} = 25.30 \mu\text{m}$, while for the fine fly ash fraction the mean particle size is $d_{50} = 5 \mu\text{m}$. In comparison to paper sludge ash, for deinking sludge the distribution is shifted towards coarser particle size (the mean particle size for the coarse fly ash fraction is $d_{50} = 78,05 \mu\text{m}$, while for the fine fly ash fraction is $d_{50} = 5 \mu\text{m}$). The results show that a more fibrous sludge (as deinking sludge) produced larger ash particles. For deinking sludge, leaching analysis (not reported here) performed on the fly ashes indicate that generally the inorganic fraction is not water-leachable. For Na and K, scarce solubility is observed for both the fly ash streams.

² Another important finding of the experimental test runs concerns the impact of the moisture content. It was observed that upon firing of paper sludge with higher moisture content, the particle size distribution is shifted towards smaller particle size. High moisture content may reduce the volatilisation of ash-forming constituents (Latva-Somppi,1998).

4.5 Toxic trace metal partitioning

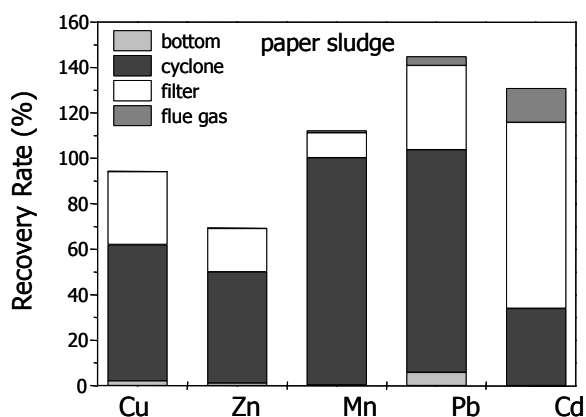


Figure 7a: Trace metal partitioning for paper sludge

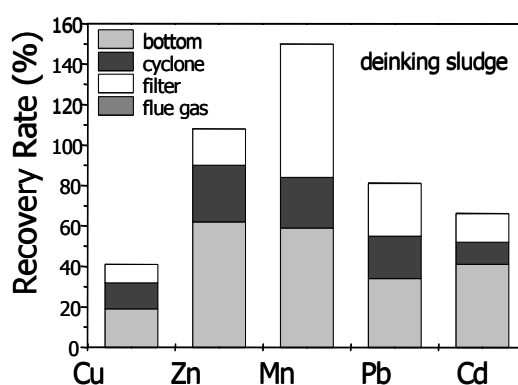


Figure 7b: Trace metal partitioning for deinking sludge

Paper sludge

Total recovery rates and mass partitioning in the ash output streams for the elements Cd, Pb, Zn, Mn, Cu are reported in the **Figure 7a-7b**.³

Figure 8 shows the results of the equilibrium calculations. In the figures, reported from literature, the stable condensed phases for Cu, Zn, Pb, Cd are calculated as a function of temperature for paper sludge system. Information on stable gaseous species at 500 °C is reported as well (Coda et al, 2001).

Pb : The recovery rate exceed 100% and this may be due to an underestimation of the Pb content in the fuel. It is important to note that Pb is mostly recovered in the coarse ash fraction. 5 % of Pb is found in the bottom bed ash, while the vaporised fraction at the stack is 3%. The equilibrium calculations show that at typical fluidised bed temperatures (880°C), Pb exists in gas phase as $PbCl_2$. Formation of condensed Pb phase, as olivine, occurs at temperatures about 700°C. At 500 °C, only 64 % of Pb is present in gaseous phase as $PbCl_2$.

Cd: Experimental results show that Cd is depleted in the bottom ash, indicating a total devolatilisation at bed temperatures. Unlike the other metals under investigations, Cd fraction emitted from the stack is 10% of the total fuel amount. Cd recovery in the fine ash fraction is very high. In optimal consistence with the experimental findings, indicating the existence of high Cd gaseous concentrations at low flue gas temperatures, condensed phases are not predicted to form up overall the whole range of temperature up to 400 °C.

³ The load variation does not typically impact the trace metal emission, whose variation is usually within the range of the standard deviation error for the measurements. This result is applicable to all the fuel blends under investigation.

Cu The amount of Cu emitted in the flue gas is less than 0,45 % ; the fraction of Cu found in the bed is also negligible. In agreement with the experimental findings, equilibrium calculations indicate the absence of condensed phases at 880°C. Formation of condensed phases (tenorite) is predicted to begin at about 620 °C; at 500 °C, the condensation is almost completed, and the share of Cu existing as CuCl₂ in the gaseous phase is only 2.84 %. Cu is enriched slightly in the fine fly ash fraction, while its recovery occurs at higher temperatures along the flue gas path, as confirmed by the equilibrium calculations.

Zn : Zn fraction in the bottom ash represents 1,3 % and the fraction emitted in the flue gas 0.03%. At bed temperature a Zn-silicate is formed, but a highest fraction is devolatilised. Formation of olivine phase and of the silicate phase 2ZnO*SiO₂ is predicted to begin at 800 °C. At 500 °C, the predicted fraction of vaporised Zn is 0,80%.

Mn: Mn is almost entirely recovered at high shares in the coarse fraction. Mn is slightly depleted in the filter and not detected under vaporised form in the flue gas.

Ni and **Cr** were not detected in the flue gas for paper sludge combustion. Equilibrium calculations indicate that, at 880 °C, Ni is forming only solid silicates phases. At the same temperature, 85% of Cr is under a form of oxides in the solid solution. Equilibrium calculations show also that 100% of Ni and Cr are condensed at the cyclone temperature (500 °C).

For coarse and fly ash fraction water leaching was performed. The results showed that all the elements, with the exception of Cd were not water-leachable.

Deinking sludge

Pb is depleted in the bottom ash and mostly found in the fly ash streams; Pb is enriched in the fine fly ash. The share of vaporised Pb is 0.04 %, much lower in comparison to paper sludge.

Cd: the total recovery is quite low and this may be due to an overestimation of the content in the blend. Cd is slightly depleted in the bottom ash, but enriched in the fine fly ash: unlike paper sludge, Cd share in the flue gas is very low (0.4 %).

Cu total recovery is unfortunately quite low ; a major share is found in the coarse fly ash. Cu was not detected in the flue gas.

Zn the share found in the flue gas is quite low (0.07%) ; Zn is highly recovered in the coarse fraction.

Mn was not emitted in the flue gas; the highest share is found in the fine fly ash

Ni and **Cr** were not detected in the gas phase.

For coarse and fly ash fraction water-leaching was performed. The results showed that trace metals were not detected under water-soluble form for all the fly ash-streams.

For the paper sludge system, the available equilibrium calculations report that the toxic trace elements under investigations are bounded under silicate form, and this is also consistent with the fact that they were not water-leachable. This effect occurred with high probability to a similar extent for deinking sludge. However, differences in Cl content may affect also the behaviour of some trace metals. On the basis of the measurements at the stack, we conclude that the amount of toxic trace metals under vaporised forms is much higher for paper sludge than for deinking sludge. Cl has a strong influence on the volatility of the elements (Verlhust et al, 1996). Comparison of equilibrium calculations and experimental partitioning show that especially Cd may exhibit enhanced volatility. Equilibrium predictions indicate a high volatility for Pb, too- due to formation of $PbCl_2$ - but to a minor extent than Cd.

Despite the high fuel concentrations of toxic trace metals, for deinking sludge generally low risk can be expected with respect to the enrichment of the toxic trace metal in the fine particulate and fine fly ash, as toxic trace metals appear to be generally enriched in the coarse ash fraction.

4.6 Discussion and conclusions

Bottom ash formation mechanisms for the two fuels under investigations are different. For paper sludge, a light coating on the sand surface is formed; on reverse, deinking sludge combustion will provoke the occurrence of sintered ash particles, which may lead to the formation of jetsam agglomerates, and eventually to defluidisation. In a large-scale boiler, characterised by higher fluidisation velocities, the bed agglomeration phenomena due to the formation of jetsam agglomerates are expected to be more limited.

XRD analysis performed on fly ash samples shows that the original mineral structure of paper sludge had almost disappeared. The calcium carbonate and the alkali have been transformed into alkali and ca- (aluminum) silicates as reacting with Kaolinite.

The resulting fly ash particles are coarser than the coating or fillings in the clay, suggesting that agglomeration of sintered particles occurred. What might happen is that the ash particles partly melt during the combustion process; the appearance of a molten structure may enhance the agglomeration phenomena. It is important to point out that ash melting phenomena occur upon combustion of both deinking sludge and paper sludge, however, to a different extent: for paper sludge combustion, it affects only the formation of fine fly ash, while having no consequences on bottom ash or bed agglomeration.

The appearance of a molten phase depends, however, on the fuel particle temperature, and this is difficult to estimate. It is also likely that, a high-volatile, porous fuel, like paper sludge undergoes attrition and comminution phenomena, giving raise to multitude of char fragments of small size, which are easily entrained out of the bed, and reaching much higher peak temperatures. (Chirone et al, 1991). This topic will be examined in detail in chapter 6.

The presence of melting may be associated to the ternary system Ca/Al/Si; high concentration of Ca in the fuel shifts the system towards low melting point (Latva-Somppi, 1998). Ash melting for the system K_2O -CaO-SiO₂ has been reported at typical fluidised combustion temperatures, in dependence of the system composition (Öhman et al, 2000).⁴

The fly ash agglomerates of sintered particles can provide a high surface area for gas-to-particle transformation routes. The occurrence of a high surface area in the ash enhances either the gaseous species condensation on solid particles or the chemical reactions.

Risk of corrosion for alkali chlorides deposits is expected to be higher upon paper sludge combustion than upon deinking sludge combustion, due to the higher share of soluble alkali in the fly ash. .

The amount of toxic trace metals under gaseous forms at the stack is higher for paper sludge combustion than for deinking sludge. Except for Cd, whose volatility is strongly influenced by high Cl content, the other toxic trace metals are likely to be bound to a high extent under silicate forms in the fly ash.

The high unleachability of the toxic trace elements of interest may be also due to their encapsulation as silicates in the ash matrix, therefore depleting their vaporisation (Kozinski et al, 1994; Rink et al, 1995). This effect, not comprised in the equilibrium calculations, may be also an explanation for the behaviour observed. This is of great importance for the environmental impact of the ash with respect to disposal.

⁴ Due to a lack of thermodynamic data for several intermediate phases in the system K/Al/Si/Ca, multiphase equilibrium calculation cannot be used in this case to accurately determine the melting behaviour. (Sandelin, 2000b)

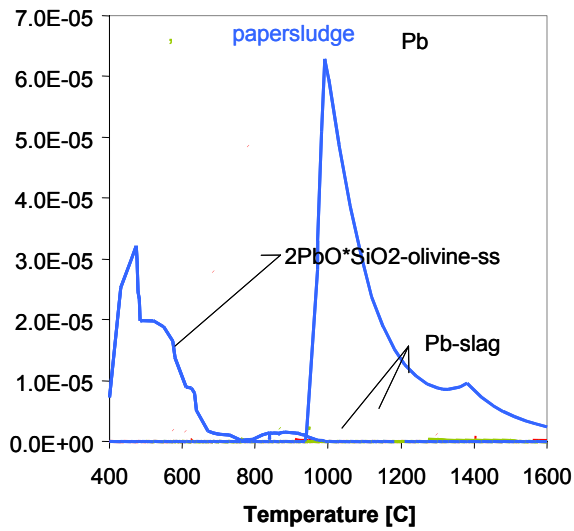


Figure 8a

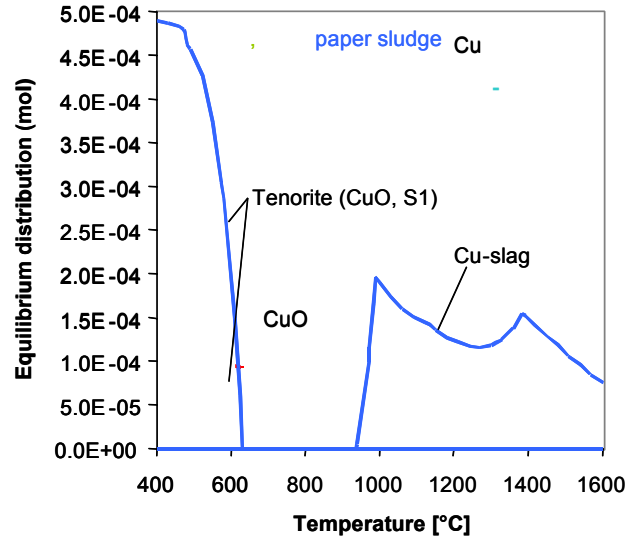


Figure 8b

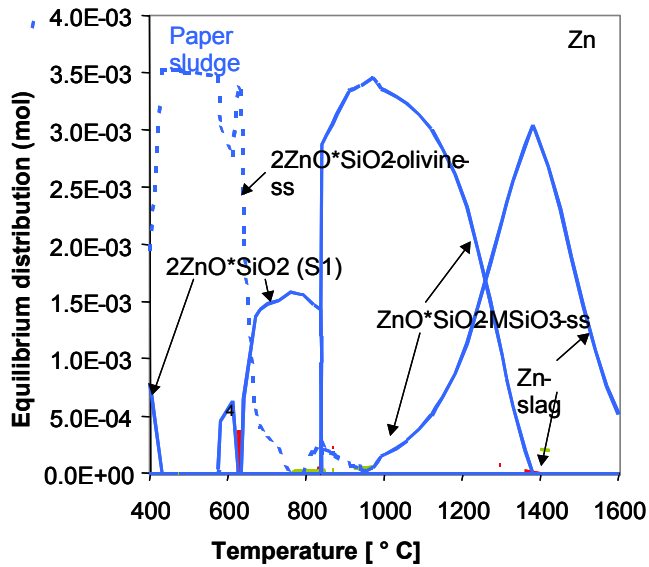


Figure 8c

Figure 8a-8b-8c: stable condensed phases for the system paper sludge+ bed material. Elements: Pb, Zn, Cu.

5. THE INFLUENCE OF ADDITIVES ON THE BEHAVIOUR OF CHLORINE AND RISKY ELEMENTS IN BUBBLING FLUIDISED BED COMBUSTION OF PAPER SLUDGE

5.1 Introduction

This part of the study was motivated by the acquisition of detailed knowledge on fate of Cl and other risky elements upon FB combustion of paper sludge, and on Cl interactions with paper sludge mineral matter constituents. To this purpose, chlorine behaviour upon different dosage of additives (Al/Si-based and Ca-based) has been studied. High chlorine content in the paper sludge is due to the presence of extraneous material, like plastic. Calcite and Kaolin are, on reverse, main constituents of the paper fillers.

The present investigation provides information that could be applied to the optimisation of the combustion behaviour of high-Cl content fuels. The investigation has been performed in the framework of research activities related to the optimisation of the Cl behaviour when waste-containing feedstocks are incinerated in FB combustors. Chlorine recovery and enrichment of Cl, Na, K, Ca, Al, Si in coarse and fine fly ash were studied experimentally with the TSF and with another 30 KWth BFB reactor, electrically stabilised, (located at VTT, Technical Research Centre of Finland, Jyväskylä), also capable of reproducing the particle residence times existing in full-scale BFB plants. In this way the behaviour of several biomass-, high-Cl content fuel blends upon additive-assisted combustion could be compared.

The experimental approach followed to investigate the fate of Cl is based on ash mass balances, on gaseous HCl-discontinuous measurements, and on chemical characterisation of fly ash and bed ash fractions. A brief section discussing the estimation of risk due to chlorine enrichment on fine fly ash, and possibilities for further investigations, closes the chapter.

5.2 Additives

Table 1 shows the chemical composition of the additives utilised in the study. Kaolin, bauxite and calcite were chosen as additives. The forest industry, producing part of its energy by BFB boilers, uses kaolin in paper manufacturing. Bauxite is the starting compound in aluminium production. Bauxite has been utilised to check the impact of Si on Cl capture. The kaolin contained only small concentrations of other compounds than Al_2O_3 and SiO_2 , but the silicate content was much higher than that of industrial bauxite. Although pure bauxite (Al_2O_3) does not

contain silicate, the industrial bauxite used here contained silicate as impurity. The particle size of the additives is as follows:

Kaolin particle size: $d_{90} < 12 \mu\text{m}$; $d_{50} < 6 \mu\text{m}$; $d_{10} < 2 \mu\text{m}$. Bauxite has a quite narrow particle size distribution, as $3 \mu\text{m} < d < 7 \mu\text{m}$. Calcite d_{50} is = $25 \mu\text{m}$.

Negligible influence of particle size in the range $32\text{-}75 \mu\text{m}$ up to $70\text{-}1000 \mu\text{m}$ on the rate of chlorination of calcined limestone has been reported (Matzukata et al, 1996).

Generally the additive negligibly influenced the ash mass partitioning, and, for paper sludge combustion, the fractions of bed ash, cyclone ash and filter ash were the same as reported in chapter 4. This corresponds to the typical case of an industrial BFB boiler, where approximately 90% of the totally fed ash is recovered as fly ash.

The dosage of additives represents the main variable of this investigation. Dosage is defined as the ratio between the mass flow of additive and mass flow of fuel ash. In the following figures, the X-axis values represent the dosage of additive. The reference test corresponds to: air staging/air ratio = 0/1,6; bed temperature = $850 \text{ }^\circ\text{C}$.

Additive	Al ₂ O ₃	SiO ₂	Sum1	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	PO ₃	S	d ₅₀ (μm)	Sum2
Kaolin	23.2	66.0	89.2	<0.1	1.1	1.5	0.1	5.2	0.0	-	18	4,5
Bauxite	84.9	3.4	98.3	<0.1	0.2	1.3	<0.1	0.3	0.2	-	10	2.0
Limestone	0.4	2.0	2.4	57.0	0.5	0.1	0.1	0.1	0.1	-	25	57.9

Table 1 : Chemical composition of the additives

5.3 Al-based additives

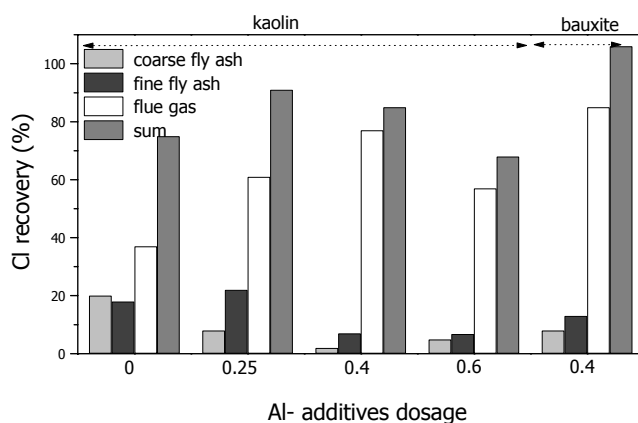


Figure 1: Recovery of Cl in fly ashes and flue gas for paper sludge with kaolin and bauxite addition. X-axis values represent the dosage of additive (unit: mass flow of ash).

5.3.1 Cl partitioning

Figure 1 shows the partitioning of Cl between coarse fly ash, fine fly ash, and flue gas. Cl concentration in the bed was negligible, showing a complete devolatilisation upon additive dosage. The results show a clear transfer from fly ash to flue gas when the dosage of kaolin was increased; in addition, a relatively larger amount of Cl was recovered in fine ash than in coarse ash. In a similar way, bauxite addition to paper sludge provoked a shift of Cl compounds from fly ash to flue gas.

5.3.2 Enrichment of risky elements

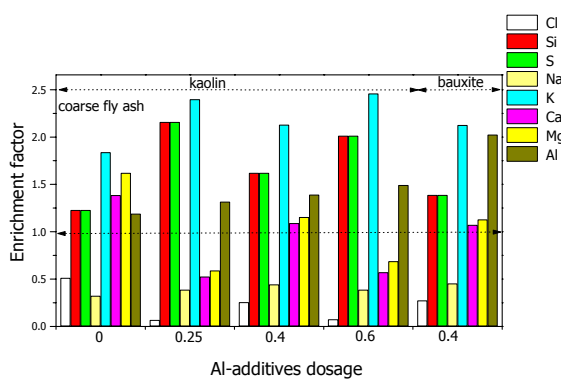


Figure 2a Enrichment factors for main ash-forming elements for kaolin and bauxite addition. Coarse fly ash

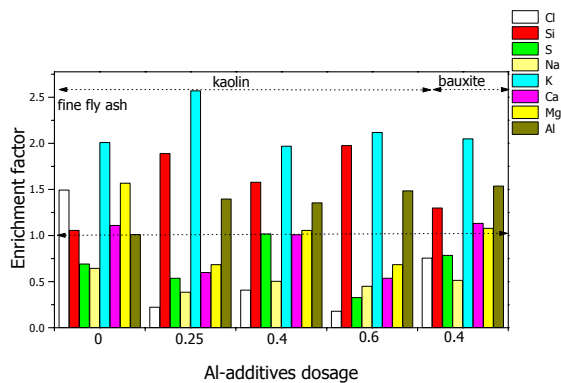


Figure 2b Enrichment factors for main ash-forming elements for kaolin and bauxite addition. Fine fly ash

to coarse and fine fly ashes; the enrichment was stronger than with kaolin as bauxite contains more Al than kaolin; correspondingly, enrichment of Si in the coarse ash fraction was lower. K and Na enrichment values were, instead, strengthened for the coarse ash fraction only.

A study of the ash composition has been done to check the influence of the additive dosage on the partitioning of the other ash-forming constituents. For this purpose, the variable enrichment factor, as defined in the 3rd chapter, has been evaluated for the coarse and fine fly ash. The results are reported in **Figure 2a–2b**. As expected, addition of kaolin caused a sharp decrease in the Cl concentration in the fly ashes, while Al concentration increased; the increase was in the same range in the coarse and in the fine particles. A slight decrease was found on the enrichment for K and Na upon addition of kaolin. The generally high values of K enrichment may be explained by interactions with fragments of bed causing the formation of K-silicates (sand contains 3,5 % as K₂O).

Upon bauxite addition, Al was enriched

An enrichment trend in sulfur was observed for the coarse ash particles when dosing additives, while for the fine ash particles the trend is less clear. The ash particle size distribution was impacted by the additive dosage to a very low extent.

Figure 3 shows the SEM analysis for the fine fly ash particles sampled upon kaolin addition. The fine ash structure resembles the very loose agglomerated ash structure, which had been observed for paper sludge combustion without additive (see chapter 4th). EDX-point analysis, effected on single, small, round agglomerating particles, in the range of 4-6 μm , indicated a high enrichment in Si-Al and K, probably associated to the fine fragments of paper sludge ash, reacting with kaolin; the occurrence of Si-Ca structures has been detected.

Likewise, SEM analysis for fly ash sampled after bauxite addition (here not reported), indicates that even the coarse ash fraction is highly composed by very small particles (about 2-3 μm particle size) that are adsorbed on the larger one. These very small particles are composed mostly by Ca-Al-Si, as it is possible that they derive from fused ash particles due to ash sintering.

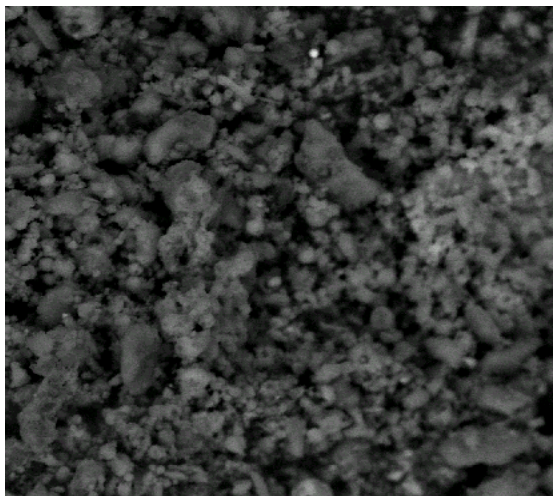


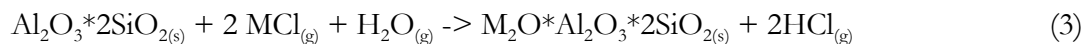
Figure 3: SEM analysis of fly ash sampled upon addition of kaolin (fine fly ash fraction)- SE*600 magnification

Similar experiments aiming at evaluating the impact of the Al-based additives have been performed in a comparable 30 kWth BFB combustion facility, located at VTT's research centre in Jyväskylä, Finland. Combustion test runs of wood/agricultural waste blends were performed, using kaolin and fly ash as Al-based additives; upon combustion of wood/plastic waste (PW) blends, the variation of the total amount of PW in the fuel blends has been associated to the variation of Al-dosage, as PW contains high Al amounts. Extensive comparison of

the additive-based tests campaign is described in published referred work (Coda et al, 2001). The results obtained with the other fuel blends indicate the analogous shift of Cl concentration from fly ash to flue gas, and a similar enrichment of Si, Al in the coarse fly ash fractions, as experienced when firing paper sludge upon increasing of the total Al-dosage.

5.3.3 Discussion

The comparison of the partitioning data and enrichment factors suggest that the reactions



between alkali chlorides and Al-silicates occur upon addition of kaolin. When high content-chlorine fuels are burned, alkali metals are released at bed and freeboard temperatures as alkali chlorides (Valmari, 2000). The results from equilibrium calculations, reported in 3rd chapter, confirmed that this would also occur upon paper sludge combustion. The alkali chlorides may react with Al-containing additives in the combustion chamber or in the path from freeboard to cyclone, as reaction (3) may be favored at typical temperature range 800-600 °C.

The molar ratio $X = (\text{Na} + \text{K}) / \text{Cl}$ for coarse and fine fly ashes was evaluated. **Figure 4** shows its variation against the net Al_2O_3 dosage. This ratio can be useful to follow the shift of alkali from alkali chlorides to larger molecular compounds. Ratios >1 indicate that alkali are bounded with other compounds, while if the ratio $=1$ it would mean that all the alkali were in chloride form.

It can be noticed that in the coarse and in the fine fly ash the ratio X increases with the dosage of Al-based additives. The generally increasing values of the ratio X upon Al-dosage indicated an

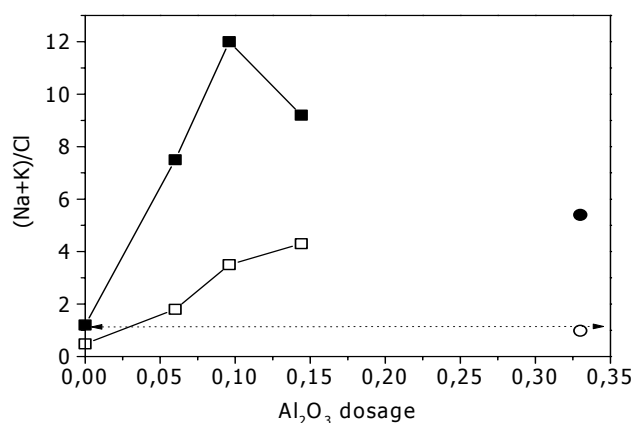


Figure 4 Molar ratio $(\text{Na} + \text{K}) / \text{Cl}$ in coarse and fine fly ash as a function of the net Al_2O_3 dosage. Closed symbols are for coarse fly ash; open symbols for fine fly ash. Legend: square: kaolin addition; circle: bauxite addition.

enhanced formation of other compounds rather than alkali chlorides. This confirms that the additive tends to react with vaporized alkali chlorides, forming other compounds at their expenses, transferring them from vapor to solid phase. As far as the results obtained at VTT are

concerned, ratio X increased in the coarse ash, but remained roughly constant despite the decrease of the concentrations of Na, K, and Cl, indicating negligible contribution of other alkali compounds to this ash fraction; these differences have been associated to the finer particle size distribution of the baghouse filter at VTT's facility. These results prevailed upon Al-assisted combustion of wood/agricultural waste (Coda et al, 2001). Increasing the plastic waste in the blend, on the contrary, suggested the occurrence of other mechanisms than described.

Water leaching analysis carried out for the coarse and fine ash paper sludge combustion, illustrated in **Figure 5**, showed that the addition of kaolin sharply decreased the concentration of water-soluble Na and K. This was a further indication of the enhanced presence of alkali aluminium-silicate forms at the expense of alkali chlorides. Alkali solubility was higher at lower kaolin dosage. Alkalis were more water-leachable in the fine than the coarse fly ash. Generally, K was less water-soluble than Na. However, results for K in the coarse ash fraction may also be affected by interactions with bed material. For the ash generated upon addition of bauxite, the results indicated a minor impact on leachability in comparison with kaolin addition. This suggests the presence of a form (such as M-Al oxide) that is more water-soluble than M-aluminium silicate. Enhanced formation of HCl with bauxite addition points to the occurrence of reaction (4).

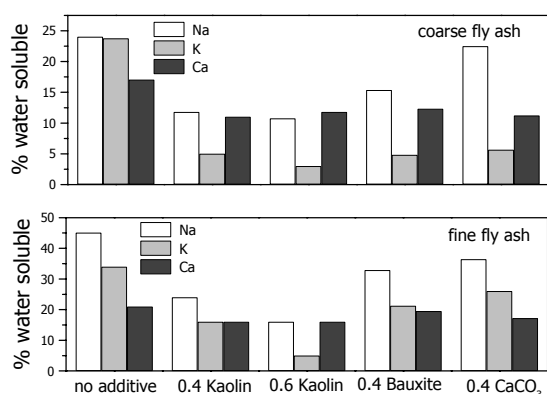


Figure 5 Impact of additive on the water-soluble fraction of Na, K, Ca for coarse and fine fly ash.



SEM analysis also confirmed the differences of morphological structure of the ash recovered for bauxite and kaolin addition.

Ca-leachable fraction does not significantly change with the additive dosage. This result, associated to the negligible variation of Ca enrichment values, suggests that Ca speciation and sulphur-retention reactions are not affected by the Al/Al-Si reactions.

5.4 Limestone addition

5.4.1 Cl partitioning and enrichment of the risky elements

Chlorine concentration in fly ashes increased with limestone dosage, as shown by **Figure 6**. This was mainly associated to the increased Cl recovery in the coarse fly ash, while Cl concentration in the fine fly ash remained roughly constant. HCl measurements showed that the residual Cl was

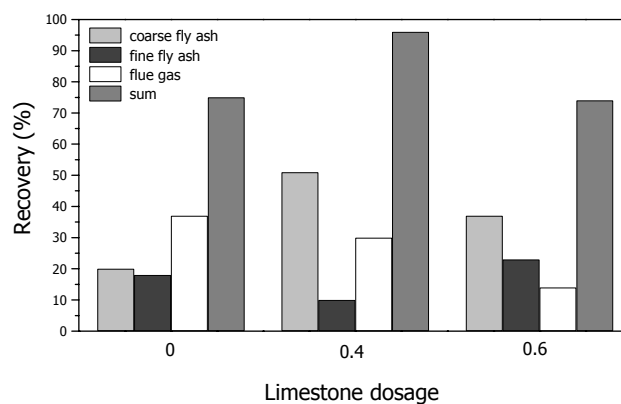


Figure 6 Recovery of Cl for limestone addition

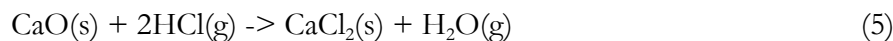
in gaseous form, and that HCl concentrations decreased with limestone dosage.

Analysing the variation of ash composition upon limestone addition by means of the enrichment factor (**Figure 7**), it can be noticed that higher Cl enrichment occurred mostly for the coarse fraction. Ca enrichment increased both in the coarse and in the fine fly ash. The results suggest that coarser fly ash is more affected by the additive than fine fly ash.

Sulfur recovery increased when adding limestone. A weak decrease was measured for the coarse fractions but the effect is probably due to dilution. K and Na enrichment clearly decreased with dosage in the fine fly ash and were roughly constant in the coarse fly ash. Al and Mg enrichments decreased in both fly ash streams for all fuels due to dilution. Si enrichment can be considered roughly constant. It is evident that Al, Mg, Si partitioning are not affected by limestone addition.

5.5 Discussion

The reaction between CaO and HCl:



occurs mostly at low temperatures (550-700 °C), so that the formation of dechlorination reaction products is likely to occur in the flue gas path between freeboard and cyclone.

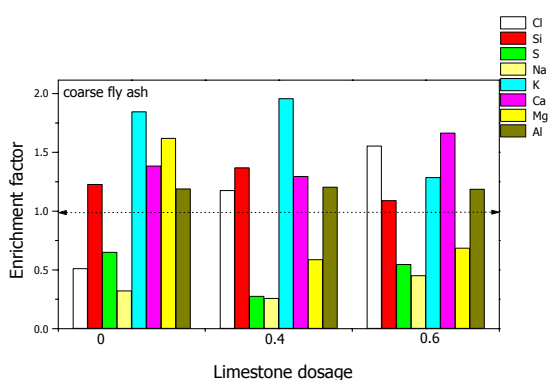


Figure 7a Enrichment factors for main ash-forming elements for limestone addition. a) coarse fly ash

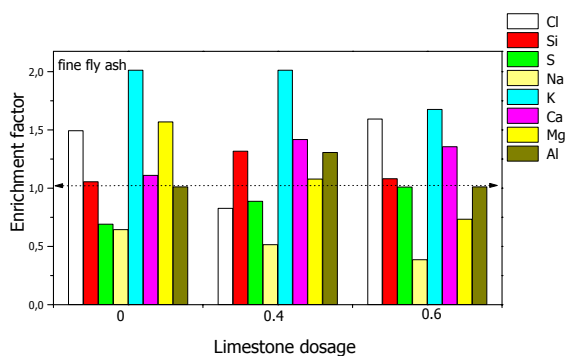


Figure 7b Enrichment factors for main ash-forming elements for limestone addition. a) fine fly ash

A clear effect was found of increasing efficiency of recovery of HCl with increase of HCl concentration (Liu et al, 1999; Bu et al, 1999). On this basis, limestone may assist in reducing HCl emissions and enhance recovery of Cl in the coarse particle fraction.

Upon combustion of paper sludge without additive, the value of the molar ratio $(\text{K} + \text{Na} + 2\text{Ca}) / (\text{Cl} + \text{S})$ is = 1, indicating that alkali sulphates and chlorides are the most likely compounds under which the S and Cl are bounded, for both coarse and fine fly ash. Upon addition of limestone, the molar ratio $(\text{Na} + \text{K}) / 2\text{S}$ in the fine fly ash was = 1. On the basis of these results, we suggest that limestone addition provokes a shift from alkali chlorides to alkali sulphates. Additional studies with XRD are needed to confirm this observation.

Leaching analysis, shown in **Figure 5**, performed on samples of paper sludge combustion assisted by CaCO_3 , suggests indirectly that the coarse fly ash fraction, where most of the chlorine is recovered, contains less leachable compounds than the fine fraction. The water-leachable portion of Na and Ca for the coarse and fine fly ash fractions is not significantly affected by the

addition of limestone. In contrast, K becomes less water-soluble upon limestone addition. Indirectly, this suggests that there is weaker formation of alkali chlorides in the coarse fraction and that Cl may be bound in large molecular compounds.

5.6 Critical remarks and further investigations

The results of the experimental investigations proved evidence of the effectiveness of the reactions between Al-containing additives and the alkali chlorides originating from paper sludge under BFB combustion; the results could be analogously extended to other low-sulfur blends, as suggested by similar test campaigns performed with biomass fuel blends (Coda et al, 2001). It has been suggested that when kaolin was added, the dominant reaction pathway involves the production of alkali-aluminium silicates, mainly transferred to the coarse fly ash due to the occurrence of high-temperatures reactions, while, upon bauxite addition, the contribution of other reactions, e.g. leading to the formation of Al-oxides or, generally, more soluble compounds than Al-silicates, is instead prevailing. At the same dosage level, bauxite was slightly more effective than kaolin, but further investigations are required to assess it.

The paper additive-mineral size (Latva-Somppi, 1998) are much finer in comparison to the additive used for these experiments, as the range for coating clay is 0,2-2 μm and for filler clay 0.2-20 μm ($d_{50} = 3 \mu\text{m}$). Under the assumption that the global reaction rate may be dependent on the particle size in case of internal diffusion-limited regime or in chemical reaction limited regime, the kaolin in the fillers will be presumably much more reactive than the additive, and as consequence, the impact on Cl release may be much stronger.

The reduction of Cl concentration in fly ash provoked by the addition of Al-compounds is significant for fine fly ash particles, which are more harmful to the boiler furnace in terms of deposit formation and corrosion. Attention must be paid if the increase in HCl emissions that occurs may limit the portion of waste-based fuel that can be used in co-combustion, as HCl concentrations may exceed the planned limit for co-incineration in the EU -30 mg/Nm^3 @ 6% O_2 - (Coda et al, 2001).

The fuels under investigation were low-sulfur blends, and therefore the sulphation reactions were not dominating. The competition of the Al-based reactions with the sulphation reactions still requires further investigations, especially with high-sulphur content fuels.

While kaolin tends to release HCl, calcite tends to retain it. The results have proven also that limestone depletes HCl formation and increases Cl binding in the fly ash. The results of the experimental campaign with Al/Si-based additives indicate that the capture of the vapour phase alkali with gettering material could require an additional HCl separation from the gas phase. The

results obtained under limestone addition suggest further investigations concerning the optimisation of Cl release and alkali vapour capture in relation to the process parameters.

As reported in chapter 2, investigations concerning the removal of toxic metal compounds have assessed that solid sorbents could be effective also in the removal of gaseous trace metals from the flue gas (Uberoi and Shadman, 1991; Ho et al., 1997). So far, these investigations have been carried out mostly simulating flue gas environments at high temperatures. Although chemical absorption reactions between metal vapours and a number of sorbents have been observed, the complex chemical interactions between multi-pollutant environments and the solid ash substrate originating from biomass or waste combustion need, however, to be investigated in combustor reactors.

6. IMPACT OF PAPER SLUDGE ADDITION ON ASH BEHAVIOUR: COAL-STRAW BLENDS AND COAL-BLENDS

In this section the ash behaviour under co-combustion conditions will be analysed. Two main fuel blends have been investigated: 1) coal/straw- based; 2) coal- based. Paper sludge replaced the fossil fuel up to a share of 25 % on an energy basis. When firing straw, the straw share (50% on an energy basis) has been kept constant. The analysis of the behaviour of the coal/straw-based blends is broader, taking also advantage of the comparison of BFB/CFB mode. One fundamental aspect, on which the comparison of the two fuel blends is based, is that their fuel chemistry differs to a large extent.

6.1 Fuel characterisation

Fuel characterisation for coal, straw is reported in **Table 1**. For the sake of comparison, the corresponding properties for paper sludge (already listed in chapter 4) are reported as well.

Co-combustion experiments were performed using a high-volatile Colombian bituminous coal

Fuel	Coal (wt %)	Straw (wt %)	Paper sludge (PS) (wt %)
Moisture	3,4	12,2	8,5
Ash (db)	11,4	2,6	3,9
C (db)	66,7	45,2	45,2
H (db)	4,7	4,7	6,3
N (db)	1,31	0,4	0,11
S (db)	0,80	0,09	0,07
O (diff) (db)	15,09	47,01	44,42
LHV (MJ kg ⁻¹)	29,3	17,4	19,1
Ash forming elements	(%ash)	(%ash)	(%ash)
K ₂ O	2,1	28,4	1,25
CaO	2,4	7,2	17,17
MgO	1,4	1,8	4,55
Na ₂ O	0,5	0,4	4,79
Al ₂ O ₃	19,5	0,9	6,1
SiO ₂	61,6	36,4	35,57
Fe ₂ O ₃	8,2	0,7	1,56
Cl	0,02	0,35	0,32-0.09
Trace elements	mg/kg	mg/kg	mg/kg
Hg	<0.06	<0.06	0.06
Mn	40	25	10
Pb	1.7	0.5	15
Cd	0.17	0.08	0.07
Cu	7	3	20
As	2	<0.1	0.5
Ni	10	6	10
Cr	14	10	14
Zn	20	20	150
Particle size (mm)	1-4	3-9	3-9

Table 1: Fuel and ash analysis of the coal, straw and paper sludge used during the co-combustion tests.

and Danish straw as main fuels. Straw and paper sludge have higher moisture content than coal. Straw, as typical (Lin et al, 1997; Evald, 2000; Hansen et al, 1997) contains less ash than coal, but higher K and Cl amounts. Aluminum and silicates are, on the contrary, the main ash-forming constituents in the coal. Replacing coal with paper sludge when co-firing increases the total concentrations of Ca, Na and Mg in the ash. **Figure 1** shows that replacing paper sludge with coal shifts the total ash composition, decreasing Si, S and enhancing mostly Cl, Na and Ca total content. Paper sludge and straw contain less nitrogen and sulfur in comparison to coal.

The concentrations of the elements for the analyzed coal are covered in the typical range for these trace metals (Clarke et al, 1992). If compared to paper sludge, the heavy metal

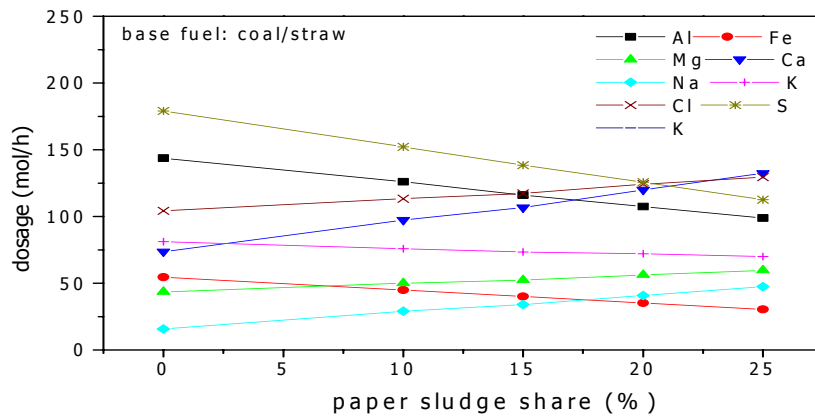


Figure 1: shift of the ash composition by replacing coal with paper sludge in coal/straw-based blend

content in the straw is low. High concentrations of Mn in coal and straw have been measured. Since straw contains generally low concentrations of toxic trace metals, it has been difficult to accurately determine their amounts in the fuel. Pb, Cu, and Cd concentrations in straw are however in the same range as reported in recent works (Evald, 2001).

Round robin tests for trace metals were performed with the other partners of the project JOR3-CT97-0191 (Aho et al, 2001). The characterization has been performed by means of different techniques (AAS, NAA, ICP, XRF). The results of the Round robin tests are reported in the **Table 2a, 2b, 2c**, each partner utilising a different ash characterisation technique.

The results for coal show a very good agreement with each other. For straw, the results are also generally in agreement with the exception of Cu. By means of ICP, higher concentrations of Mn and very low concentrations of Ni were measured. Differences exist for Pb as well. For paper sludge, a fuel which is highly inhomogeneous by nature, the more remarkable differences are noted for Pb, Cd and Zn. Cu concentration measured by Midtkraft is always higher than the other measurements.

coal	IVD	VTT	IMPC	Midtkraft
Hg	<0.06	<0.06	0,031	0,053
Mn	40	40	23	
Pb	1.7	1,5	1,5	3,8
Cd	0.17	0,15	0,1	0,113
Cu	7,3	7,0	4,5	117,5
As	2	2,0	1,6	<2
Ni	10	6	6,8	
Cr	14	14	8	
Zn	20	20	30	32, 33

Straw	IVD	VTT	IMPC	Midtkraft
Hg	<0.06	<0.06	0,009	0,010
Mn	25	40	220	
Pb	0.5	1,5	1,7	8,4
Cd	0.08	0,08	0,1	73,33
Cu	3	3	3	117,5
As	<0.1	<0,1	0,2	<2
Ni	6	10	<0,1	
Cr	10	14	8	
Zn	20	20	28	44,33

Paper sludge	IVD	VTT	IMPC	Midtkraft
Hg	0.06	0.06	0,038	0,035
Mn	10		35	
Pb	15	7	13	22
Cd	0.07	0,07	0,1	1,167
Cu	20		21	205
As	0.5	0,5	1.3	<2
Ni	10		5	
Cr	14		5	
Zn	150		74	167

Table 2a, 2b, 2c: Results of Round Robin tests for paper sludge, straw and coal. Concentrations in mg/kg dry fuel. (IVD, Germany- used AAS; VTT, Finland- used graphite furnace AAS for Cd, As, Pb, and XRF after ashing at 550 °C for Ni, Cr, Cu, Zn, Mn; IMPC: Imperial College Of Science, UK- used ICP after wet ashing and microwave digestion analysis; samples characterised by means of ICP were previously milled and sieved to the fraction of 100-200 µm; Midtkraft, Denmark- not specified).

6.2 Leaching analysis

The fuels were characterised with respect to the speciation of their elements. This has been performed by means of leaching analysis. The idea of this method is that a qualitative correlation can be found between how elements are leached out from the fuel and how elements are released during combustion. The extraction method results, reported in **Table 3**, show that most of the elements in paper sludge and straw are both water-soluble and acid-soluble at higher shares in comparison to coal. Most of the elements are not washed out in coal and are retained in the residue.

It is important to notice that the leachability of Al and Na from paper sludge is much higher in comparison to the same constituents for coal. The fraction of total Al amount that is water-soluble is 24% for paper sludge, 38,1% for straw, and only 1,2% for coal. The presence of alum as paper coating might comprise for the relatively high solubility of Al in the paper sludge, which

should be theoretically water-insoluble if it was all bounded under form of Al-silicate. Na from paper sludge derives mostly from deinking agents (NaOH, NaSiO₃).

The results for Ca show a comparable degree of mobility in the coal and paper sludge. Potassium in coal has been reported to be mostly associated with aluminosilicate minerals and therefore water-insoluble (Hodges et al., 1989). The form in which sodium occurs in coals has been the subject of several debates, with the opinion prevailing that (Hodges et al., 1989) it is bounded as a hydrated form. For straw, instead, alkali are leached to a high extent, as well as Cl and S. Similar

	coal			straw			Paper sludge		
	WS	AS	AI	WS	AS	AI	WS	AS	AI
Ca	24,5	73,3	53,2	31,9	94,2	0,8	50,1	66,66	41,2
Si	0,1	1,4	97,3	44,5	53,6	81,2	13,9	34,7	75,3
Na	22,1	44,1	69,8	100,1	129,	<0,01	67,1	80,1	30,1
K	3,1	8,34	94,2	64	94,6	11,0	53	80,6	21,2
Cl	0.1	-	<0,01	110,1	-	<0,01	32,3	-	<0,01
Al	1,2	5,9	94,1	38,3	51,8	56.3	24,2	88,3	10,1
S	36,1	6	43,0	54,6	46,0	3,8	54	30	6,4

Table 3: Inorganic analysis by the chemical extraction procedure. (wt%). Note: WS: water soluble; AS: acid soluble; AI: acid insoluble (residue)

results for straw related to the water-leachability have been reported (Skrifvars et al., 2001).

6.3 Mass balances and ash partitioning

Before looking into details the behavior of the single ash-forming constituents upon co-

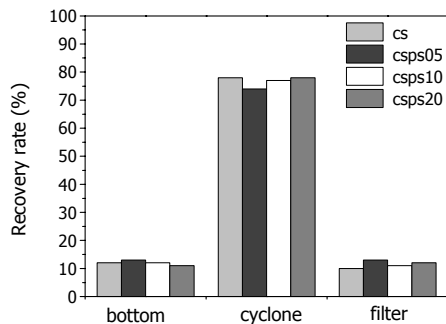


Figure 2a: Total ash partitioning under BFB conditions for coal/straw/paper sludge blends

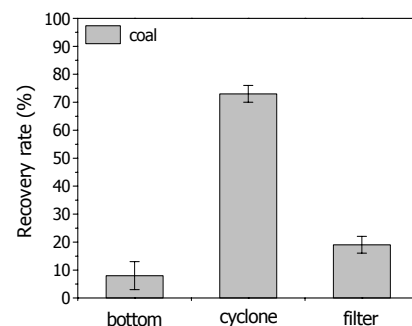


Figure 2b: Total ash partitioning under BFB conditions for coal firing

combustion, a short description of the overall mass balances is reported.

The bed removed after each test run appeared as a heterogeneous material, consisting of original bed sand particles alternated with ash (and char) particles. Unlike paper sludge firing, the minerals

were observed to remain among the bed material in two forms during the co-combustion test runs: 1) captured in single particles, too large to be entrained by the flue gases; 2) forming an ash layer on the surface of the sand surface (coating). The results of BFB mode test runs, reported in **Figure 2a**, show that for coal/straw/paper sludge blends, the share of total ash is:

- 12% (± 3) of the total ash-forming constituents is recovered as bottom ash,
- 78% (± 5 %) is entrained from the bed and collected as cyclone ash
- 10 % (± 3) forming fine ash and collected as filter ash.

This partitioning is hardly affected from the share of paper sludge in the blend. These values correspond to the typical ash partitioning in a large-scale BFB boiler. For the sake of comparison, it can be noticed that similar values of partitioning were found upon coal combustion, as reported in **Figure 2b**, with a larger ash fraction recovered in the filter.

6.3. 1 BFB combustion

The partitioning of the single elements is shown in **Figure 3a, 3b, 3c, 3d, 3e, 3f, 3g**. Bottom ash is totally depleted in sulfur and chlorine. The amount of magnesium in the bottom ash is also quite small compared to the other ash-forming elements. Potassium, Calcium and Aluminum are captured efficiently in the bed and the fraction found in the bed increases when the share of paper sludge in the fuel blend is higher. Sodium percentage in the bed is also significant for the fuel mixtures that include straw. For the case of coal firing, (**Figure 4**) sulphur and chlorine are also completely devolatilised from the bed; a low share of alkali is found in the bed; and a high share of Ca is recovered in the bed (about 10%).

For BFB combustion mode, the residual ash particles fraction in the bottom represents about 15 % of the total bottom ash. As reported in chapter 4, upon combustion of paper sludge as a single fuel, no residual, single particles had been found in the bottom ash. For coal firing, the amount of coal ash on the bed coating comprises about 30-35 % of the total bottom ash for BFB fluidisation mode. This shows that the residual ash particles derive mostly from the coal combustion.

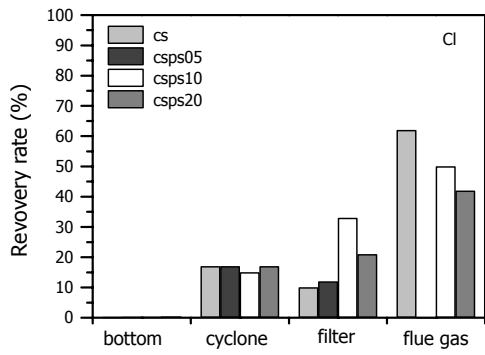


Figure 3a

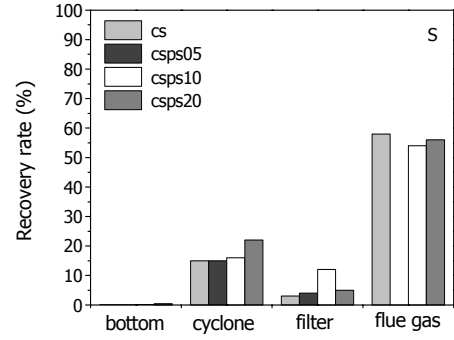


Figure 3b

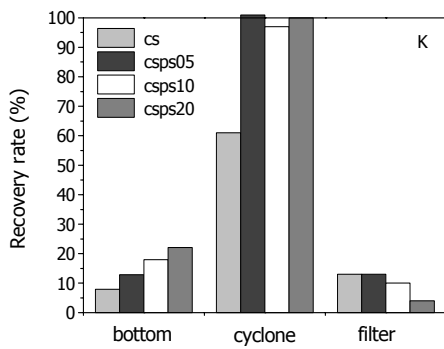


Figure 3c

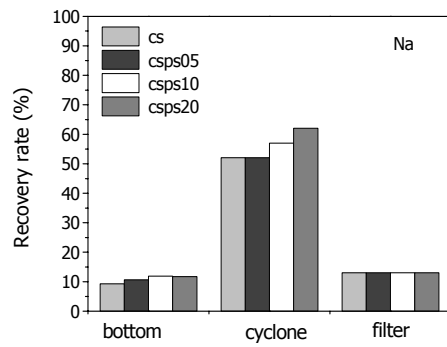


Figure 3d

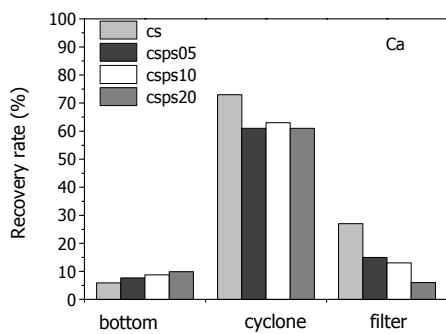


Figure 3e

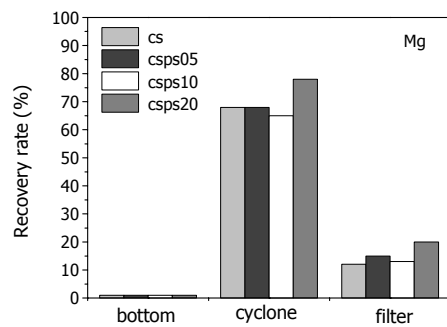


Figure 3f

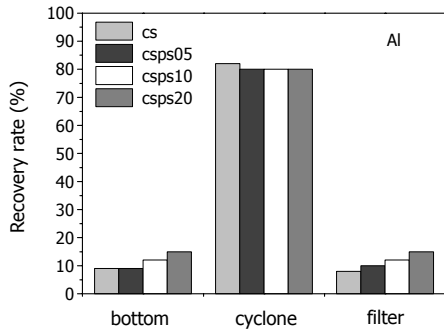


Figure 3g

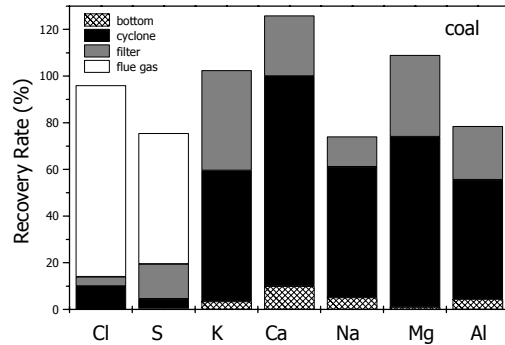


Figure 4: Partitioning of elements between the various ash streams- coal firing.

Figure 3a-3g: partitioning of ash elements between the various ash streams for the coal/straw/paper sludge blends under BFB conditions. Elements: Cl-S-K-Na-Ca-Mg-Al

6.3.2 CFB combustion

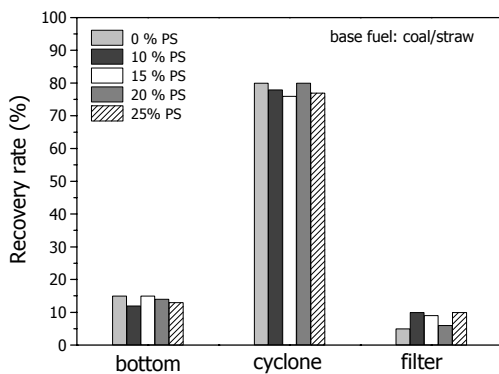


Figure 5: Total ash partitioning for CFB conditions

As shown in **Figure 5**, under CFB combustion mode, the fraction of the total ash forming the bottom ash (return leg and bed ash) is about 15 % (± 5 %); the fraction found as cyclone ash is 80 % (± 3 %), while the fraction collected as filter ash is 5% (± 2 %). Under similar test runs conditions, for coal combustion, the following partitioning results were reported: bottom ash: 10%; cyclone ash: 75%; filter ash : 10%. The results of CFB combustion test runs, reported in **Figure**

6a, 6b, 6c, 6d, 6e, 6f, show that, similarly to what observed for BFB conditions, chlorine escapes the bottom bed; while sulfur is highly recovered in the bed- test runs were performed with a Ca-based additive. Aluminium is slightly enriched in the bottom bed, while, unlike BFB conditions; K and Na are slightly depleted. Mg (and Ca only in some cases) appears slightly enriched in the bottom ash. Under CFB combustion mode, the occurrence of single, residual ash particles is also remarkably higher in comparison to BFB combustion conditions (representing about 30%- of the total bottom ash).

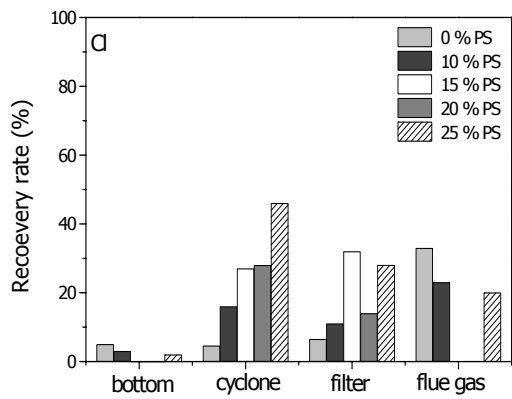


Figure 6a

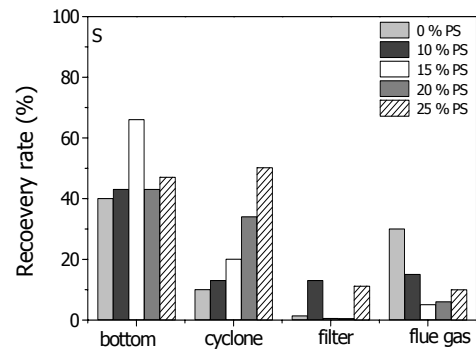


Figure 6b

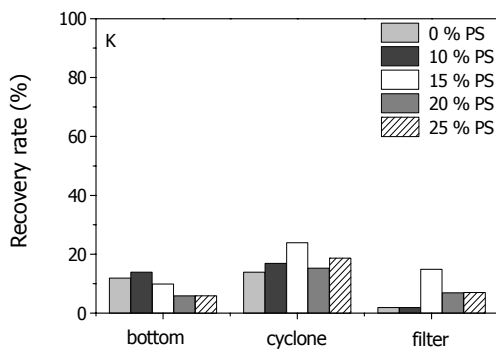


Figure 6c

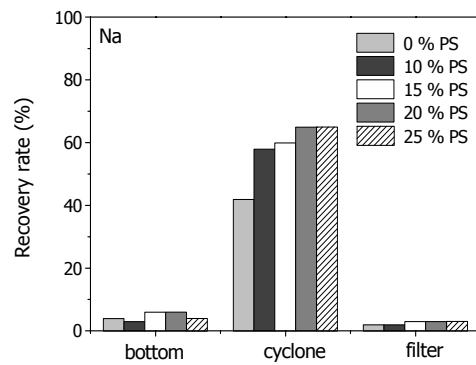


Figure 6d

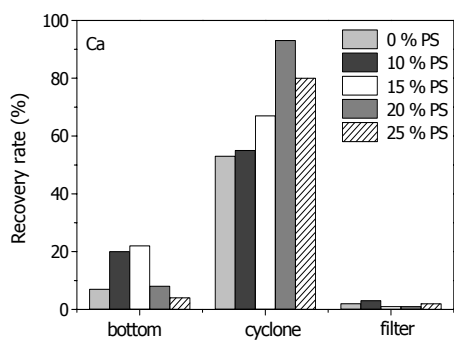


Figure 6e

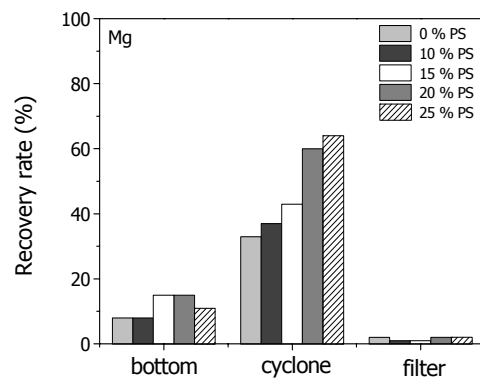


Figure 6f

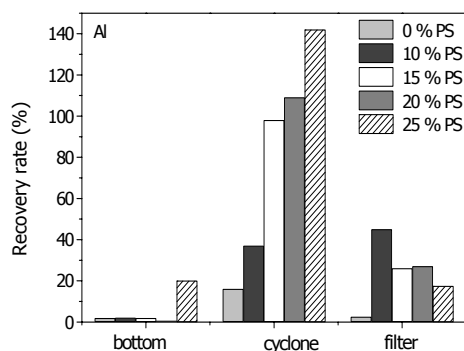


Figure 6g

Figure 6a-6g: Partitioning of ash elements between the various ash streams for the coal/straw/paper sludge blends under CFB conditions. Elements: S-Cl-Ca-Na-K-Al-Mg.

6.4 Coating formation in the bottom ash and bed agglomeration

This section describes how different physical and chemical phenomena influence the formation of coating and bed agglomeration. Most experimental data available are for the blend coal/straw/paper sludge. Additional tests performed with coal/paper sludge blends support the understanding of the governing process.

6.4.1 BFB combustion

Bed agglomeration-related phenomena will be analysed in detail for the case of coal/straw/paper sludge blends under BFB combustion mode, where these phenomena were detectable to a larger extent than for CFB combustion mode. On the basis of the BFB results, the analogies and the differences for the CFB systems will be described.

For coating it is meant the formation of a homogenous ash layer on the surface of the particle of the bed material, caused either by particles collision or ash volatilisation/condensation phenomena. The formation of an ash layer on the bed particle surface, causing an increase in the particle stickiness, due to partial melting, has been identified as a major mechanism for the occurrence of bed agglomeration (Manzoori, 1992, Skrifvars, 1998, Lin, 1997, Öhman and Nordin, 2000). The analysis of the coating bed material is helpful to acquire information whether a fuel blend shows bed agglomeration tendencies. The characterisation of the coated sand

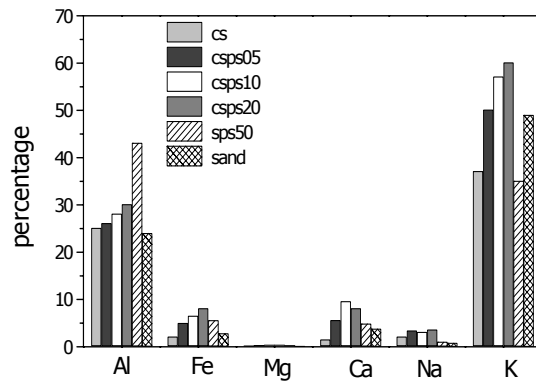


Figure 7: Coating composition in dependence of the fuel blend composition- coal/straw- based blends- BFB combustion mode

particles was the starting point of the study.

Figure 7 reports the share of ash forming elements in the sieved bed material, normalised under silica-free basis. The main variable is the share of paper sludge in the fuel blend. For the sake of comparison, coating composition of blends of straw/paper sludge (50%/50% on an energy basis) and the pure sand composition have been reported as a reference. The comparison between the various test runs is made possible, since operative variables like test run duration time, and mean bed temperature -880 °C- have been kept equal.

From **Figure 7** it is clearly seen that the concentration of aluminum, potassium and calcium in the coating increases as the share of paper sludge is increased in the fuel blend. Similar trends are also observed for iron and sodium in the mixtures including coal. Magnesium is not found in the sieved bed material to a large extent. It is likely that the share of Fe found in the coating is due to vaporisation of FeS_2 from coal particles. It is interesting to note that the test run without coal seem to differ from the others with respect to the trends observed for iron, calcium, sodium and potassium. Aluminum concentration in the coating is also much higher in comparison to the fuel blends containing coal. Sulfur and chlorine were not detected on the coated bed particles.

The impact of operative parameters, like bed temperature, and bed height, on the coating composition has been studied when firing a blend containing 10% of paper sludge. These results are reported more extensively elsewhere (Coda et al, 1999), and only some details will be summarized here. Increasing the bed temperature has little impact on the enrichment of the inorganic constituents of the ash coating, suggesting that the bed temperature in the tested range

does not markedly affect their transformation. The impact of air ratio (varied in the range 1.2-1.8) and of the bed height on the coating composition was also negligible.

Visual inspections of the bed showed that an increased share of paper sludge in the fuel blend enhanced the formation of agglomerated fragments. Highly friable clusters were already found when firing a share of 10% of paper sludge. When firing 20% of paper sludge in the fuel mixture, several, isolated fragments of agglomerated structures were found after the removal of the bed material. The agglomerates consisted typically of a melted core on which other coated, single sand particles had adhered.

After inspection of the TSF, some agglomerates of about 3 cm length were found, i.e., about 1/3 of the inner diameter of the bed. During the experiments, no sign of alteration of pressure drop (initiating the start of the defludization process) was measured.

The SEM image of the agglomerated sand surface (**Figure 8**) shows the presence of a) a glassy, melted structure, b) a porous structure. The glassy structure is associated to melting, while the

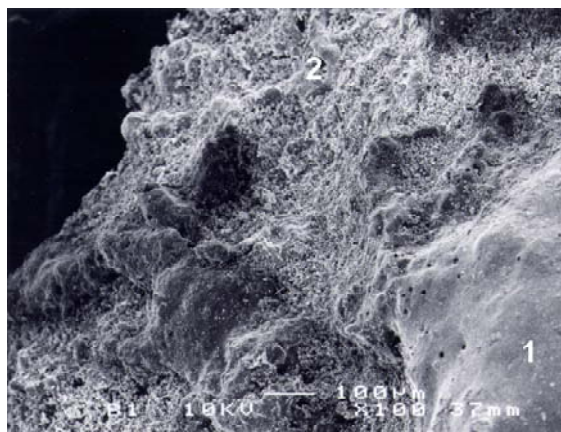


Figure 8: SEM picture of sand agglomerate

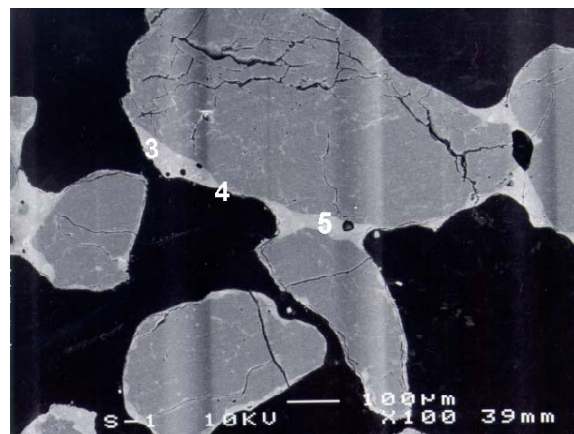


Figure 9: SEM picture of a polished agglomerate sample

porous structure may be reconnected to the incorporation of burning-char fragments, which get attached to agglomerated particles.

The passage between the two structures is abrupt. The EDX analysis, effected on different points of the glassy sand surface, shows the presence of a complex structure enriched with a significant amount of Al, Ca and K. On the porous structure, also small amounts of Cl and Na are detected, indicating their origin from a burning fuel particle. **Figure 9** shows a SEM image of a cut polished section of bed material for the test case where 30% coal, 50% straw and 20% paper sludge were co-fired ¹. The black background in the image is epoxy in which the bed sample was

¹ The chemical composition of the points 1-2 in Figure 8 and 3-4-5 in Figure 9, corresponding to the same numbers in Figure 14, can be found in literature (Coda et al, 1999).

mounted. The darker gray scale shows the original bed material and the lighter gray color deposited material. At first eye, the deposit seems like a homogenous material; however, careful inspection reveals that there are also some inhomogenities. The deposited material also seems to form "necks" or "bridges" between original bed sand particles. The white numbers in the picture mark the position of the EDX-point analyses. The analysis of the "neck" (point 5), and of the coating as well, reveals high Ca, Al, K. concentrations. The coating is not porous, but rather smooth and compact.

Mathematical calculations, not reported here, were performed according to the onion ring model introduced by Manzoori et al. (1994). The results of the calculations show that, due to an increased ash deposition rate on the particles, the mean diameter of the coated bed particles

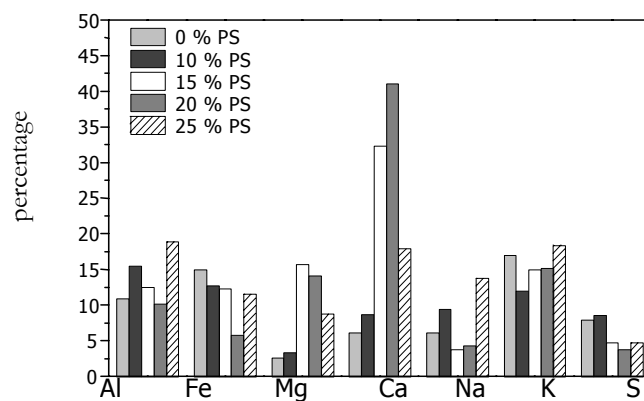


Figure 10: Variation of the coating composition – coal/straw- based blends-CFB mode

increases when co-firing paper sludge. The calculated mean layer thickness ranges between 15-20 μm for a mean bed particle size of 400 μm . This is consistent with the mean coated particle size as measured by means of the SEM microscope.

6.4.2 CFB combustion

The variation of the coating composition upon increase of the share of paper sludge in the fuel blends for CFB combustion conditions is shown in **Figure 10**. Similarly to BFB conditions, the coating is enriched in Al, K, and the enrichment is higher the more paper sludge is fired in the fuel blend. Unlike BFB firing, and due to limestone addition, the coating composition is

characterised by the presence of Ca, Mg and S.² Their occurrence on the bed particles is likely to derive from collision with the reacting limestone particles.

Comparing the coating composition and the recovery rate, it can be concluded that elements like K and Ca (and partly Na and Mg) are mostly transferred on the bed particles. They form a coating, and do not remain in the single, residual, ash bottom particles. Ca is always easier

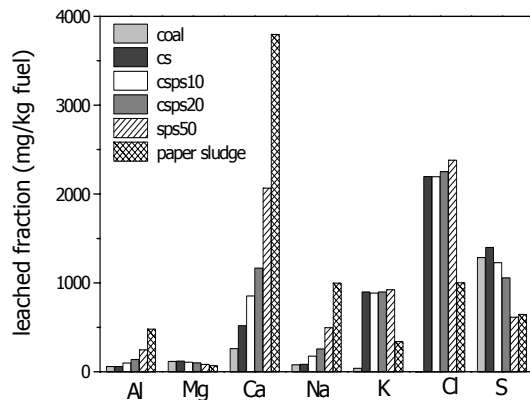


Figure 11: Leached amounts of the coal/straw – based fuel blends. Calculations based on the leaching data taken from Table 3

transferred to the melt than Mg (Sandelin, 2000). Bed agglomeration tendencies increased with the share of paper sludge in the fuel blend. Visual inspection of the bed, after the completion of the test-runs, showed that clusters in the size range 0,5-0,7 cm were formed. Visual inspection showed that the clusters were less reacted than those found under BFB conditions. Formation of agglomerates under CFB conditions occurred to a less extent than under BFB mode; reasons may be the higher fluidisation velocities and the smaller size range of bed particles. Chemical analysis performed on the clusters showed their high content in Al, K, and Ca. This suggests, in consistence with what was observed for BFB conditions, the occurrence of molten phases of K, Al and Ca silicates.

6.4.3 Comparison with the leaching behaviour

As it has been mentioned at the beginning of the chapter, the use of the leaching analysis for ash characterization is that a qualitative correlation can be found between how elements are leached out from the fuel and how they are released during combustion. The results of the leaching analysis are correlated with the coating bed results.

Figure 11 shows the result of this exercise where the experimental leached amounts of Al, Mg, Ca, Na, K, Cl and S, as reported in **Table 3**, have been re-calculated to obtain the leached amounts in 1 kg of a fuel mixture.

From the figure it can be observed that the leached amount of aluminum, calcium, and sodium clearly increase as the share of paper sludge increase. Except for the leached amount of

² According to equilibrium calculations, additional dosage of limestone with a Ca/S=2 shifts only slightly the total system towards higher ash melting temperatures this leads to a slight theoretical reduction of the

potassium from coal and paper sludge, the amount of magnesium and potassium seems almost constant. Most of the chlorine originates from straw and the leached amount increases only slightly when paper sludge is added. Very little chlorine is leached out from the coal sample.

If we compare the results of the leaching analysis with the coating composition, some similar trends can be found: the increased fraction of Ca, Al, K, Na in the coating when co-firing, and the increase of the leached fraction of the same elements in the fuel blends. The agreement is only qualitative, as no quantitative correspondence generally exists between the amount of the leached elements and the share of the elements found in the coating. S and Cl were leached out to a great extent from the fuels but never detected on the coating of the bed particles.

6.4.4 Coating formation and leaching behaviour of bottom bed ash upon combustion of coal/paper sludge blends

Similarly to what has been observed for the coal/straw/paper sludge blends both residual, single ash particles and coated particles were found upon combustion of coal/paper sludge blends. The single, residual ash particles found in the bottom bed ash have a similar chemical composition to the mean ash composition of the fuel blend. A rough estimation suggests that the residual ash particle fraction represented about 60 % of the total bottom ash. Visual observations of the residual ash fraction suggest also that they were mostly composed by unfragmented particles, probably coming from the coal.

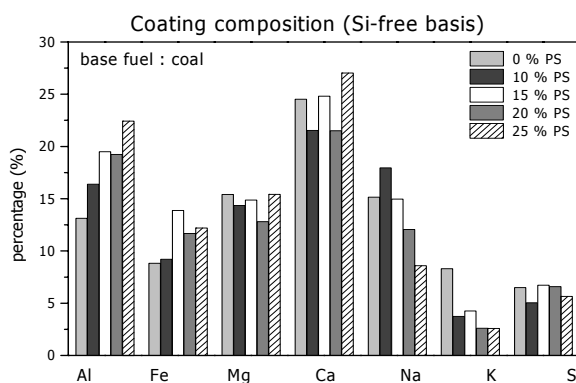


Figure 12: Variation of the coating composition – coal- based blends- CFB mode

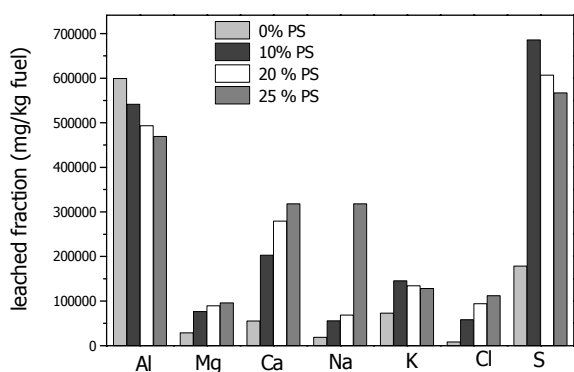


Figure 13: Leached amounts for coal-paper sludge blends. Calculations based on the leaching data taken from Table 3

Cl is totally devolatilised from the bottom bed ash. A similar result had been observed when firing coal under BFB combustion mode. K and Na are highly depleted from the bottom ash; sulfur is efficiently captured and the fraction recovered in the bed is increasing with the share of paper sludge fired. Ca and Mg concentrations are relevant in the bottom ash due to the limestone addition. Al and Fe are generally equally partitioned with respect to the total ash amount. The recovery

trends for the bottom ash are generally consistent with the enrichment of the elements on the coating surface of the bed.

Similarly to the methodology utilised for coal-straw blends, the analysis of the coating formation upon combustion of coal/paper sludge has been the basis to study the agglomeration propensity of the mixture. **Figure 12** shows the coating composition of the fuel blends re-calculated on a Si-free basis. The amounts of Al, Ca, Mg, and Fe are very high. Mg and Ca enrichment increases the more paper sludge is added in the blend. They are preferentially found in the coating, meaning that they vaporize from the fuel particles to recondense on the bed particles. K and Na concentrations in the coating decrease. Fe enrichment was observed, but this is supposed to be due to the attachment of Fe particle coming from FeS_2 in coal.

Increasing the share of paper sludge also enhanced agglomeration propensity of the bed particles. Visual observations of the spent bed material indicated that, upon co-firing, clusters were formed. Chemical characterisation of the clusters showed that these clusters are Ca-enriched, likely to come from paper sludge which contains high Ca amount. These clusters had a more porous structure than for coal/straw-based blends; they were also quite fragile. Their size derived from a continuous process of formation and destruction through bed mixing; the particles did not provoke any disturbance in the fluidisation process.

Coating material did not initiate melt. The limited thickness of the coating, up to a few microns, as calculated by the onion-ring model, suggests that attrition phenomena in the bed would break pieces from sand surface, thus limiting the maximum thickness.

In **Figure 13** the leached amounts of Al, Mg, Ca, Na, K, Cl, and S are reported, after re-

calculation from Table 3. Compared to coal system, the blends are characterised by a more “reactive” Ca, K and Na. The leaching analysis is consistent with the coating results as far as the trends for Ca, Mg concern, but less for Na, K, and Al.

6.4.5 Theoretical melting behavior of ash-forming constituents

The comparison of theoretical melting behaviour with the experimental data has been extensively reported elsewhere (Sandelin et al, 2001). The following observations are taken mostly from referred literature. The melting temperature and the total amount of melt were estimated by taking into account the fuel amount, fuel composition, bed material, and air-to fuel ratio. **Figure 14** shows the equilibrium melting curves, i.e., the total amount of melted material as a function of temperature. The equilibrium amounts in **Figure 14** correspond to the amount of fuel and bed material for one-hour operation, i.e., approximately 34 MJ of fuel and 1.75 kg of bed material. The calculations for the systems straw/paper sludge (each 50 % on an energy basis), and straw -as single fuel-are also reported.

The prediction shows that all straw-containing mixtures melt at around 765°C (that is very close to the calculated ternary melting point (769°C) of the $\text{SiO}_2\text{-4K}_2\text{O}\cdot\text{SiO}_2\text{-CaO}\cdot\text{SiO}_2$ system). From **Figure 14** it can be also seen that the amount of melt is increasing as the share of paper sludge in the fuel blend increases. The temperature of initial melting of pure coal and pure paper sludge are, on reverse, much higher. However, another melt, a liquid salt, is formed to a much less extent, at temperatures between 920°C and 976°C for coal, and between 840°C and 910°C for the pure paper sludge case.

Figure 15 shows the theoretical composition of the melt for the 30% coal, 50% straw, 20% paper sludge case as a function of temperature. It is seen that the fraction of potassium decreases rapidly as the temperature increases. The decrease is partially due to evaporation of potassium containing compounds, and to a diluting effect due to the fact that the amount of melt increases as the temperature increases.

The composition of sodium appears almost constant, with a slight decrease as the temperature is rising. Both magnesium and calcium have a maximum solubility at around 1450°C. It is also shown that calcium dissolves in the melt to a greater extent than magnesium.

The result of **Figure 15** is in **Figure 16** compared to the composition of the coated bed material, as analyzed by the SEM/EDX point analysis technique, and reported in Figure 8. Two hypothetical temperatures are included for comparison, 880°C, corresponding to the measured bed temperature during the combustion test runs and, 1420°C, corresponding to an imaginary

locally hotter region in the bed. As it can be seen from the figure, the higher temperature corresponds better with the composition for magnesium and calcium of the SEM/EDX point analysis.³

6.4.6 Fuel particle temperature: mathematical modeling

Knowledge of the fuel particle temperature during combustion may furnish useful information about the occurrence of local hot peaks in the bed. The simultaneous presence in the bed inventory of fuels with different combustion behaviour may lead to overlapping of different particle thermal histories, thus impacting the local heat transfer in the bed. Coal particles, containing high fixed carbon content, burn typically through char combustion, and slower than straw and paper sludge particles, for which the volatile combustion is dominating (Latva Somppi, 1998; Werter et al, 2000). In **Figure 17** the maximum excess temperature of a burning fuel particle is calculated as a function of the particle size. The “maximum excess temperature” is defined as the difference between the maximum temperature that a fuel particle can reach upon combustion, and the mean bed temperature. The maximum particle temperature is estimated using a steady state balance based on the Extended Resistance Equation (Essenhigh, 1988), with kinetic parameters given by Essenhigh and Mescher (1996). An important parameter for the calculation is oxygen content in the gas atmosphere (here assumed 6%).

Assuming a mean particle size of 1 mm, the calculation results show that the temperature of a burning coal particle may exceed locally the bed temperature up to 300 °C. Smaller fuel particle diameter (likely under fluidised bed conditions, due to particle comminution phenomena) may lead to excess temperature up to 600 °C.

Calculations are in agreement with reported temperature measurements on coal particles burning in a fluidized bed (Joutsenoja, 1998, Winter et al., 1997). Assuming a mean particle size of 7 mm, for example due to the larger feeding particle size of straw and paper sludge, the excess temperature is about 30 °C. At large high particle diameter, the overall reaction rate is so small, due to the increased boundary-layer-diffusion resistance, that the particle temperature is very low

6.4.7 Discussion

The comparison of the SEM pictures, the EDX analysis, and the coating chemical composition builds-up a scenario of how the agglomeration phenomena can be occurred. Bed coating may be

³ A weakness of the equilibrium model is that it excludes the interactions of aluminum in the melt. The decision to exclude the important interactions of aluminium, was taken because melting temperatures for

generally due either to physical phenomena like deposition of vaporized species (like potassium from straw, Valmari, 1999-a) or to fuel particle collision with the bed material. The coating resulted highly enriched in Ca, Al, and K. This enrichment is increasing with the share of paper sludge replacing coal in the fuel blend.

To summarize, the agglomeration process may be explained by two concomitant factors:

- 1) The presence of a coated bed material with a specific composition which is likely to undergo melting
- 2) The presence of local high temperature conditions.

It is suggested that the presence of coal when co-firing may lead to the occurrence of local higher temperature conditions, which could enhance the phenomena described above. Increased release of ash-forming constituents (like alkali) at higher temperatures may occur (Valmari, 2000); the presence of the coal may lead to higher local particle temperatures and, therefore, to high melting formation because of the propensity of the coated bed to give agglomeration, due to their specific composition. This is consistent with the occurrence of agglomerated structure in isolated, single pieces. Furthermore, combustion of blends of straw and paper sludge (50/50 on an energy basis) resulted in much lower ash deposition rate on bed particles and lower agglomeration tendencies in comparison to burning blends containing coal. Theoretical melting curves for the fuel blends show that increasing the share of paper sludge in the blend gives an increasing amount of melt, and that combustion of coal and paper sludge alone gives higher melting temperatures. This is an extremely great difference if we compare it to the results of paper sludge or coal burned as a single fuel, which did not show any agglomeration tendency at all.

It is furthermore likely that fibrous fuel particles, when burning, tend to form clusters within the bed; their fibrous nature allows the cluster to hold up various surfaces. The begin of agglomeration process may be also explained by the occurrence of local high temperature conditions, which made easier the “attachment” of the fibrous particles with other fuel particles or coated bed particles; the cluster will then (partially) melt and therefore initiate even larger agglomerates.

The equilibrium prediction at significantly higher temperatures than the bed temperature corresponds better with the measured chemical composition of the coating. This means the importance of a correct determination of fuel particle temperature under FB combustion mode to be able to predict correctly the formation of bed agglomeration phenomena.

the fuel mixtures when including aluminum were found unexpectedly low, and because data for the $K_2O-Al_2O_3-SiO_2$ system are considered "only very approximate" (Bale et al.,2001).

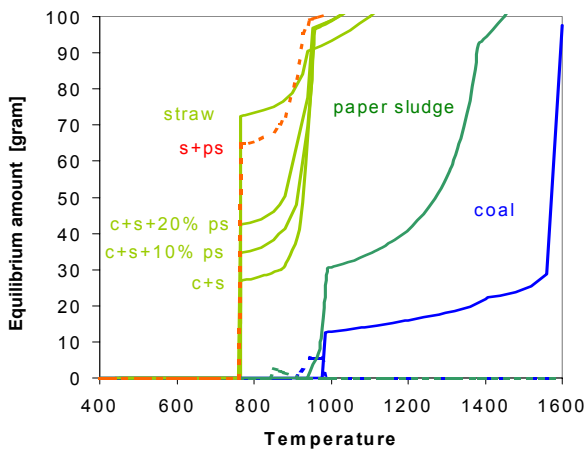


Figure 14: Theoretical melting temperatures (°C) of the system fuel blends+ sand

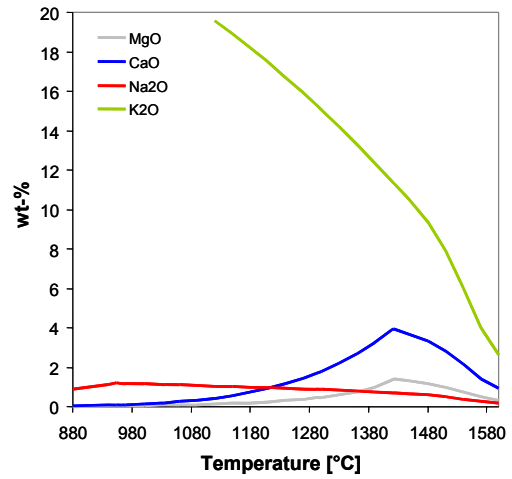


Figure 15: Predicted equilibrium composition of the melted slag phase as a function of temperature.

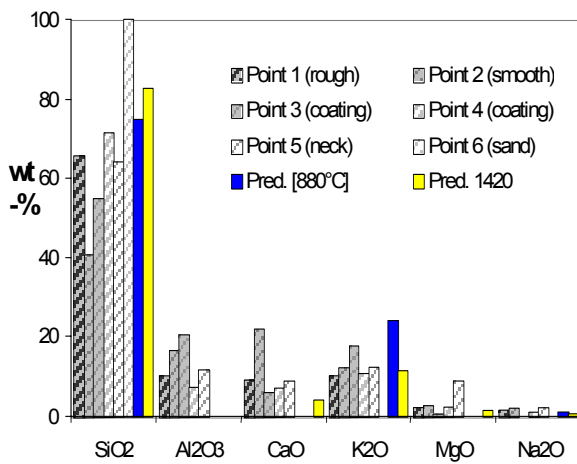


Figure 16: SEM/EDX point analysis of partially melted bed material (as in Figure 8) compared to the predicted equilibrium composition of melted

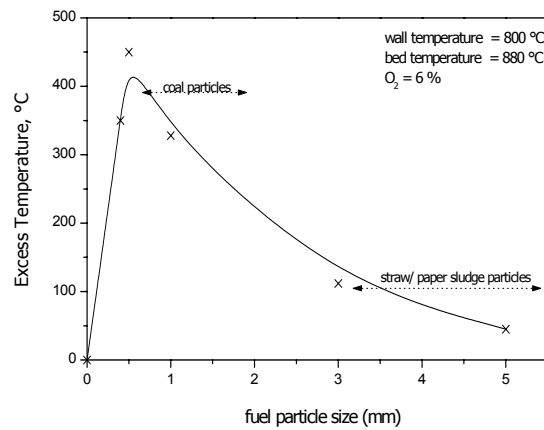


Figure 17: Maximum excess temperature

6.5 Fly ash formation and composition

An assessment of the fly ash composition is important to understand fouling phenomena that limit the boiler availability due to a decrease in efficiency

6.5.1. Review of the total ash partitioning

Coal/straw-based blends: BFB combustion

As it is shown in the **Figures 3a-3f**, increasing the share of paper sludge in the fuel blend enhances sulphur capture in the fly ash, and consistently, decreases the share of sulphur released as SO₂. Sulphur is recovered at a high share in the coarse fly ash fraction, and to a less extent in the fine fly ash fraction. In the case of coal fired as a single fuel, 58% of the sulphur has been measured as SO₂ in the flue gas in correspondence of a bed temperature of 880 °C.

Cl is captured to a large extent in the fine ash fraction, and the recovery increases with the paper sludge share added in the fuel blend; correspondingly, a decrease of the share of Cl measured as HCl in the flue gas was observed. For coal combustion, most of Cl has been found in the flue gas, -62%- and captured only to a small extent in the ashes -13%- (**Figure 4**).

For these blends, the highest fraction of alkali is associated to the coarse ash fraction. The balances closure for potassium is generally higher than for sodium.

Al and Ca are generally enriched in the coarse ash fraction. For coal firing, the highest Ca share has been recovered in the coarse fraction as well. The partitioning of Mg is not influenced by co-firing conditions. High recovery of Mg and Al in the fine ash fraction upon coal combustion had been observed.

Coal/straw-based blends: CFB combustion

Similarly to BFB combustion mode, the recovered sulfur fraction in the coarse fly ash mode is increasing when co-firing paper sludge, correspondingly to lower SO₂ emissions in the flue gas. In addition, Cl recovery is also enhanced when co-firing, and Cl enrichment in the fine fly ash is higher, in correspondence to a decrease of Cl emitted in the flue gas as HCl. K closure of the mass balance is quite poor, which is likely to be due to an overestimation of the potassium content in the straw samples. Al is highly enriched in the coarse fly ash. Generally speaking, other elements like Na, Mg, Ca are enriched with respect to the total ash partitioning in the coarse fly ash fraction, and depleted in the fine fly ash fraction when co-firing. For Mg, S, and Ca the enrichment in the coarse fly ash fraction may be associated to the formation of sulfates of Ca and Mg. (**Figures 6a-6f**).

Coal-based blends: CFB combustion

Al is enriched in the coarse fly ash fraction; the recovery of K in the coarse fly ash fraction is also

higher when co-firing, in correspondence to depletion in the fine fly ash. Mg, Ca, Na are, on reverse, equally partitioned in the fly ash streams, and their recovery in the coarse fly ash fraction is increasing when co-firing, too. The high enrichment of Si in the coarse fly ash has been associated to entrainment of fragments of bed material in the flue gas path.

6.5.2 Fly ash particle size distribution and structure

In **Figure 18** the mass size distribution of the fly ashes for BFB combustion mode is shown. Adding paper sludge to the fuel blend shifts the particle size distribution towards finer particle diameters. When co-firing 20% paper sludge, the submicron mode ash – in the range 1-0,32 μm – represented 7% of the total ash amount.

The particle size range is coarser for BFB conditions than for CFB. Ash fragmentation and attrition are usually more pronounced for CFB mode, due to the impact of the recirculation process and of the higher fluidisation velocities leads to the formation of ashes, comprising usually particles of lower- size range.

XRD analysis was also performed for these samples. KCl is the main detected phase; other alkali/chlorides and alkali/alumino-Cl based compounds were detected. Ca is bounded as complex phases of Ca/Si/ and as CaSO_4 .

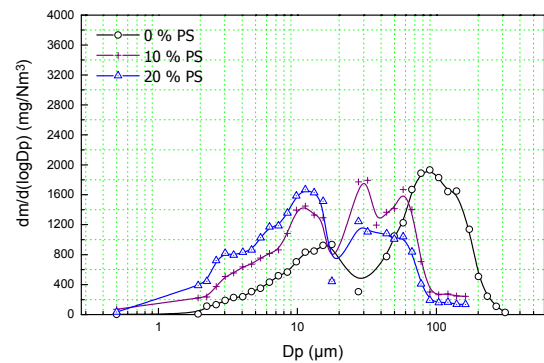


Figure 18 Particle size distributions for coal/straw- based blends – BFB mode

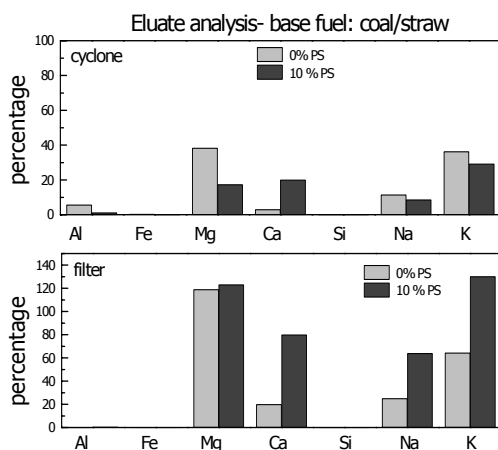


Figure 19a Ash leaching for coal/straw-based blends – CFB mode

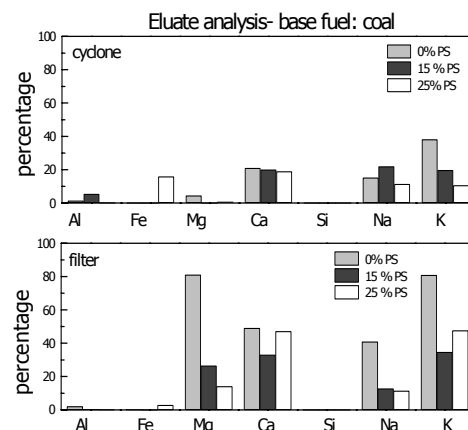


Figure 19b Ash leaching for coal-based blends- CFB mode

6.5.3 Ash Leaching

Water soluble-fractions of alkali (Ca, Na, K) in coarse and fine fly ash collected after CFB combustion experiments have been determined. The quantification of the water-soluble components gives indications of their speciation in the ash, and can be also considered as a qualitative indication to the fouling propensity. The results for coal-straw based blends are shown in **Figure 19a**. As a general result, the total fraction of soluble alkali is higher for the fine fly ash fraction than for the coarse one. Increasing the share of paper sludge in the fuel blend increases the share of leacheable alkali and Ca. This is consistent with the increasing leachable share of the same elements in the fuel samples. Chlorides and sulfates, the most soluble fraction, are expected to bind the alkali to a high share. These results confirm the qualitative description that had been given by XRD analysis.

For coal-based blends (**Figure 19b**), the share of total soluble Na and K in the fly ash decreases when co-firing. The soluble calcium fraction remains instead approximately constant. Sodium seem to be generally less water-soluble than potassium.

6.5.4 The fate of Cl and S according to the equilibrium calculations

Figures 20 and 21 show the speciation of the main condensed phases versus temperature respectively for coal system and coal/straw-based blends. The description of the coal system has been reported to compare it with the behaviour of the fuel blends.

Coal system: A low fraction of sulfur- 10%- enters in the melt as a $\text{CO}_3\text{-SO}_4$ based solution at 985 °C; 25 % of the total sulfur reacts with Ca to form CaSO_4 whose formation begins at typical fluidised bed combustion temperatures (850 °C). Formation of MgSO_4 starts at about 620 °C. At about 500 °C, the formation process of $\text{Al}_2(\text{SO}_4)_2$ begins, theoretically binding the remaining fraction of SO_2 in the flue gas, and thus completing the sulfur retention under condensed phases.. $\text{KCl}(\text{gas})$ and $\text{HCl}(\text{gas})$ are the compounds binding Cl at furnaces temperatures, while at lower temperatures, Cl gets all bounded only as $\text{HCl}(\text{g})$. Formation of condensed phases of Cl is not predicted. SiO_2 is the main component of the ash. Ca, Na and Mg form silicate-based compounds.

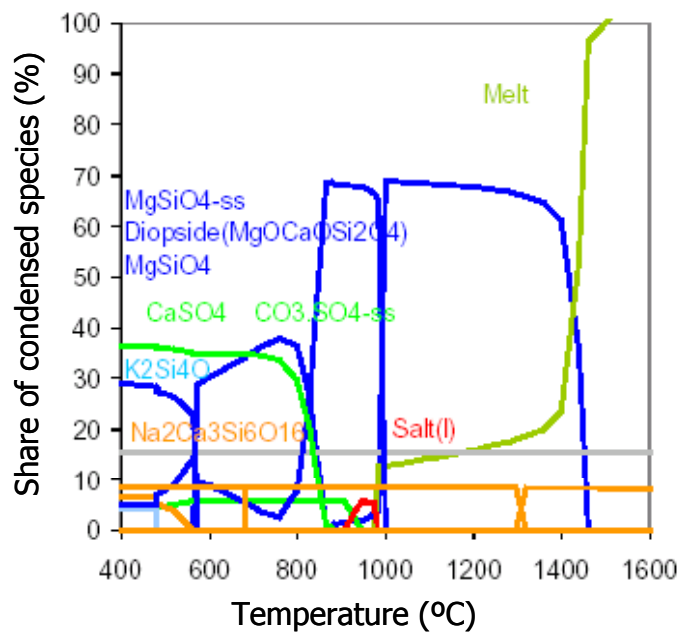


Figure 20 : Speciation of elements at different temperatures : coal system

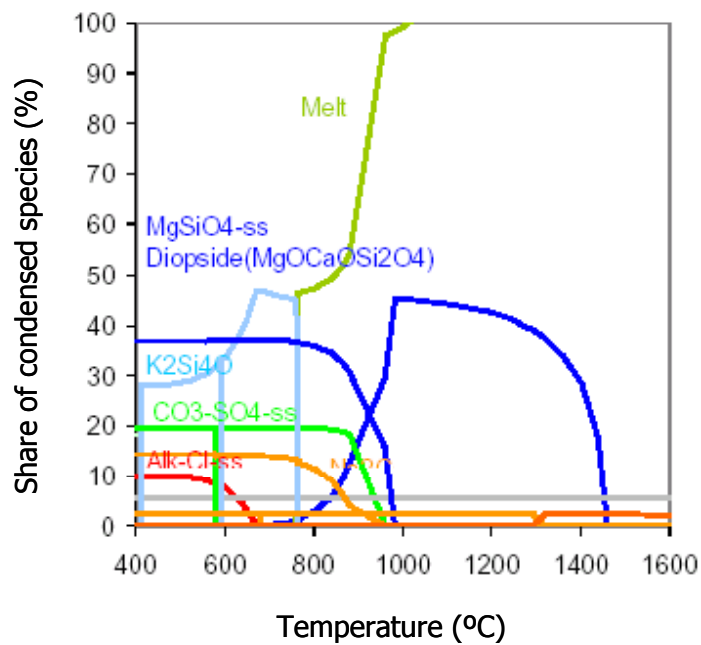


Figure 21 : : Speciation of elements at different temperatures for coal/straw/paper sludge system

Coal/straw/paper sludge systems:

At temperatures $< 900^{\circ}\text{C}$, a high fraction of alkali chlorides, which are co-existing with HCl(g) , are reacting, through the sulfation reactions, transforming Cl into HCl(g) . A remaining share of alkali chlorides condenses in the temperature range $658\text{-}669^{\circ}\text{C}$. Paper sludge addition shifts slightly the commencement of the condensation process at higher temperatures. At 400°C all Cl is bound under condensed species.

In the temperature range $954\text{-}959^{\circ}\text{C}$, sulfur begins to form solid solution of alkali sulfates, remaining as a stable phase at 400°C .

As a general important result, it may be summarised that condensation of sulfur compounds occurs at much higher temperatures than the condensation of alkali chlorides.

Equilibrium calculations predict that the formation of $\text{K}_2\text{Si}_4\text{O}$ is occurring at temperatures around 780°C . Mg, Ca is forming complex phases bounded with silicates, and Na-Ca-Silicates are formed, too. Ca is present exclusively as silicates; formation of CaSO_4 is not predicted.

Coal/paper sludge system

The speciation and the weight percentage of the main ash-forming constituents at 2 key temperatures, (880°C and 500°C), have been listed in **Table 4**. The results related to coal system and coal 75%-paper sludge 25% are reported.

At 880°C more than 75 % of the sulfur is bounded as SO_2 in the gaseous form, and gaseous concentrations of K_2SO_4 and Na_2SO_4 are quite low. CaSO_4 is formed at a temperature of about 800°C . At the same temperature, 88% of Cl is forming HCl, while the rest is bounded as NaCl and KCl (gas); the main condensed phases are olivine (mixtures of silicates) and a silicates-solid solution.

At 500°C , the share of Cl bounded as gaseous HCl (conversion of KCl and NaCl) is enhanced up to 99%; sulfur is entirely retained into solid forms, 88% as CaSO_4 , with the remaining share forming Na_2SO_4 and K_2SO_4 . Na and Mg are mostly bounded into complex silicates structures.

For the coal/paper sludge system, sulphur will not exist under gaseous compounds at low temperatures because of the increased formation of CaSO_4 at bed temperatures. On reverse, for the coal system, equilibrium calculations predict that gaseous SO_2 will react to form $\text{Al}_2(\text{SO}_4)_3$, which will be completed at temperatures lower than 500°C . K is forming K_2SO_4 , while Na is bounded to a great extent under silicates structures. The formation of Na-silicates phases begins approximately at 600°C . For the coal system, instead, Na and K are all bound into alkali sulfates.

The participation of Na to the formation of silicate phases is consistent with the leaching

analysis, showing that the share of unleachable Na is higher upon co-firing, and also that Na is less leachable than K. The recovery of sulfate is much higher in the first separator device, and this is consistent with the equilibrium calculations, showing that the condensation of alkali sulfates and CaSO_4 is occurring at furnaces temperatures.

The formation of Cl-condensed phases, is not predicted for coal/paper sludge blends by equilibrium calculations. A small share of Cl was recovered in the coarse fly ash.

XRD analysis, performed on fly ash samples, showed a clear detection of the presence of SiO_2 , and of chemical bounding of potassium and sodium in an aluminium-silicate phases (respectively muscovite and sodium-aluminium silicate hydrate); alkali sulfates were also detected; calcium is detected as Ca-Silicates and, weakly, as sulfates.

	Coal	Coal-paper sludge 25%	
	500 °C	800 °C	500 °C
S	CaSO ₄ - 7.7 % MgSO ₄ - 7% SO _{2(g)} - 85.3 %	K ₂ SO ₄ - 11.5 % Na ₂ SO ₄ – 8.8% SO _{2(g)} - 75.7%	K ₂ SO ₄ - 10 % Na ₂ SO ₄ – 2 % CaSO ₄ - 88.8%
Cl	HCl _(g) - 99.8 %	HCl _(g) -88.3% KCl+NaCl _(g) -11.%	HCl _(g) - 99.5%

Table 4: speciation of Cl and S for coal/paper sludge fuel blends

6.6 Influence of the fluidisation mode (BFB/CFB) on ash formation

The comparison of the ash behaviour under the 2 fluidisation modes (CFB/BFB) for coal/straw/paper sludge blends is allowed, as macroscopic combustion characteristics, like bed material, bed temperature, stoichiometry in the furnace and fuel blends were kept the same in both combustion modes. Furthermore, limestone addition does not notably impact the speciation and the partitioning of the inorganic constituents, under CFB mode, and therefore its influence can be neglected (Sandelin, 2000b).

Upon combustion of paper sludge as single fuel, it had been observed (as reported in the 4th chapter) that the original mineral structure of paper sludge had almost disappeared upon the combustion process. When reacting with kaolin minerals, the calcium carbonate and the alkali had been transformed into alkali and Ca- (aluminium) silicates.

The results of co-firing test runs suggest that similar mineral matter transformations occur when co-firing paper sludge with coal/straw-based blends, too. SEM-EDX analysis confirmed that the formation of the agglomerated, skeleton-type ash structure observed upon combustion of paper sludge occurred upon combustion of the blends, too.

Upon coal combustion, the formation of the fly ash particles could be associated mostly to char fragmentation phenomena. The composition of the fly ash streams upon coal combustion did not markedly change with respect to the original fuel composition. In this respect paper sludge

behaves differently from coal.

Co-firing paper sludge provokes a shift of the fly ash particle size distribution towards smaller particle-size.

The particle size of the ash was larger for BFB firing conditions. CFB mode is characterised by higher attrition rate, and ash fragmentation rate.

Bed agglomeration tendencies were observed under both fluidised modes, resulting in the formation of clusters to which other fuel and sand particles had easily adhered. Although agglomerated pieces as large as the radius of the bed were found, defluidisation did not occur. Bed agglomeration under CFB conditions occurred to a lower extent, and smaller clusters were observed. The layer structure and the chemical composition of the coated particles were similar for BFB and CFB modes, suggesting the occurrence of similar mechanisms of coating formation. As attrition and fragmentation phenomena play a more important role under CFB conditions, they may provoke a higher breaking of the layer structure of the coatings. Higher fluidisation velocities, and the lower particle size range of the bed material, are both factors delaying defluidisation.

A higher fraction of residual ash particles was found in the bottom ash under CFB conditions. This might have occurred as there were too large coal particles to be entrained. Paper sludge and straw are much lighter fuels than coal: they tend to burn on the surface of the bed under BFB. Under CFB mode, they are quickly transported to the top of the riser; however, being extremely reactive, their short residence time in the facility allows their complete burning-off.

6.7 Discussion

Sludge contains small mineral particles that, due to particle sintering, form larger ash agglomerates, resulting in skeleton-type ash. On the contrary, for coal the mechanisms of residual ash formation do not comprise the occurrence of sintering and melting; in addition, the volatilisation of mineral matter is restricted. Upon co-combustion, the fly ash will result composed by two types of ash. The formation of the porous fly ash from paper sludge is likely to have effect on the capture and condensation of gaseous species, like gaseous trace metals.

The water-insoluble alkali fraction in the ash may be composed especially by silicates, which bound the alkali in fly ash. Increasing the share of paper sludge in the fuel blend enhances presumably the contribution of silicate compounds, thus binding Na and K in the ash structure. XRD analysis, performed on fly ash samples, confirmed also that Ca undergoes both reaction of silicate formation and sulphate formation.

The comparison between XRD and leaching analysis suggests, that, upon combustion of the fuel

blends, other reactions occur than those taken into account in the equilibrium program. Experimental findings have shown that K and Na, under volatilised form at combustion temperatures, react with kaolinite to form potassium and sodium aluminosilicate compounds. This reaction mechanism, whose occurrence had been suggested upon combustion of paper sludge as single fuel, and upon combustion of paper sludge assisted by Al-based additives, is likely to occur also upon co-combustion with coal.

The formation of water-insoluble aluminium-silicates, detected by XRD analysis, was not predicted by the equilibrium calculations. Equilibrium data on the behaviour of aluminium species at low temperatures (Sandelin, 2000b) are, however, not fully reliable.

The experimental results suggest that kaolinite in the ashes should increase the gas-phase HCl and reduce the amount of Cl captured in the ash.

The occurrence of small Cl amounts in the coarse fly ash particles may be, however, associated to the formation of CaCl_2 deriving from calcite in the paper sludge. Nevertheless, CaCl_2 was not detected as species by XRD analysis.

For coal/straw/paper sludge blends, most sulphur is recovered in the coarse fly ash fraction, (and partially, under CFB mode, in the bottom ash because of the limestone dosage). Upon co-combustion, the slightly enhanced capture in coarse and fine fly ash fractions may be associated to the enhancement of a fine particle-mode fraction, on which capture of sulphur occurs either as condensation of alkali sulfate, as predicted by thermodynamic calculations, or as chemical reaction leading to CaSO_4 formation. The presence of CaSO_4 upon co-firing, detected by XRD analysis, however, has not been confirmed by the equilibrium calculations.

Alkali chlorides condensation occurs mostly on the fine ash particles at the lowest flue gas temperatures, as indicated by the high Cl enrichment for the filter ash. The molar ratio $(\text{K}+\text{Na})/\text{Cl}$ approaches 1 for the fine ash mode, for all the fuel blends under investigation. The comparison of mass balances, leaching analysis, XRD analysis, ash chemical composition, and molar ratio $(\text{K}+\text{Na})/\text{Cl}$, indicates that chlorine is enriched in the fine particles for coal/straw blends, and that it is bound as NaCl and KCl.

It is likely that the addition of paper sludge to the fuel blend enhances also condensation of alkali chlorides due to the shift of the fly ash mass size distribution towards smaller diameters and higher surface area. Furthermore, coal/straw-based blends are characterised by insufficient sulfur content for the sulphation reaction to capture stoichiometrically the total fuel alkali as alkali sulphates.

The important result of this comparative approach is that high risk associated to corrosion

induced by Cl-deposits is expected when co-firing blends of coal, straw and paper sludge.

6.8 The fate of toxic trace metals

The behaviour of trace metals upon combustion of the fuel blends will be examined in detail in the following section. Similarly to the methodology utilised to describe paper sludge combustion as a single fuel, mass-partitioning data will be explained with the support of equilibrium calculations. The total recovery and mass partitioning in the ash output streams for BFB conditions are reported in the **Figure 22a-22e** (Cd, Pb, Zn, Mn, Cu) and for CFB conditions in **Figure 23a-23e**.

Fig. 24a-24b-24c-24d-24e-24f shows the results of the equilibrium calculations. In the figures, reported from literature (Coda et al., 2001), the stable condensed phases for Cu, Zn, Pb, Cd are calculated as a function of temperature. The analysis for the following systems is reported: 1) coal; 2) coal/straw (50%/50%); 3) coal/straw/paper sludge 10%; 4) coal/straw/paper sludge 20%. Information on stable gaseous species at 500 °C is also reported. The coal system is taken into account as a reference system.

The enrichment factor E_{cic}/E_{fib} , plotted in **Figure 25a-25b** for BFB and CFB mode, represents the ratio of the concentrations in the coarse (cyclone) and in the fine (filter) fly ash, respectively. This factor has been introduced, being a qualitative measure of the relative mass that is captured on the fine ash fraction. Values of the ratio < 1 indicate enhanced occurrence of condensed species on the finer particle mode.

Figure 22a-22e: trace metal partitioning between various ash streams for the coal/straw/paper sludge blends under BFB mode. Elements: Cu-Zn-Pb-Mn-Cd. **Figure 22f**: trace metal partitioning between various ash streams for the coal system under BFB mode.

Figure 23a-23e: trace metal partitioning between various ash streams for the coal/straw/paper sludge blends under CFB mode. Elements: Cu-Zn-Pb-Mn-Cd.

Figure 24a-24f: condensed phases versus temperature after equilibrium calculations for pure fuels and coal/straw/paper sludge blends. (Coda et al., 2001) Elements: Cu-Zn-Pb-Mn-Cd.

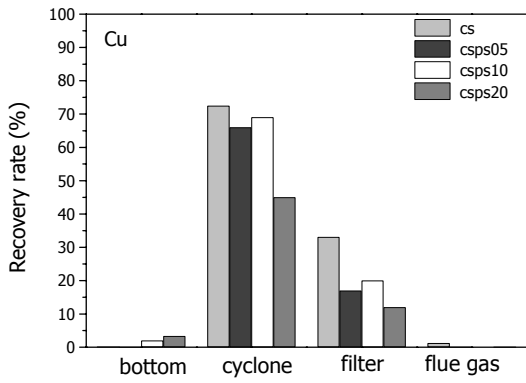


Figure 22a

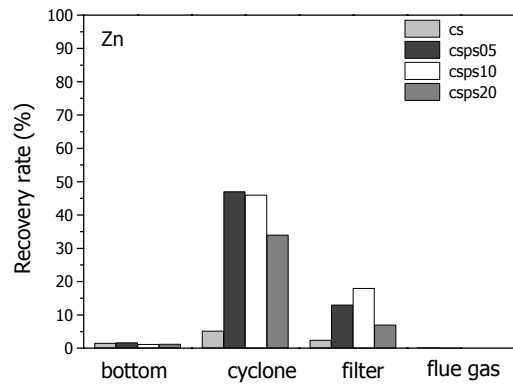


Figure 22 b

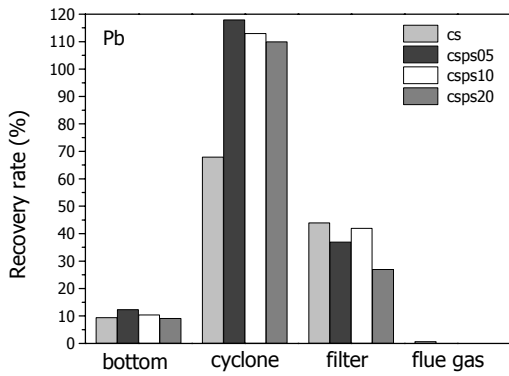


Figure 22c

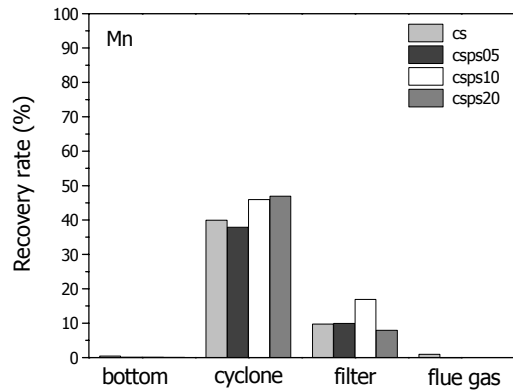


Figure 22d

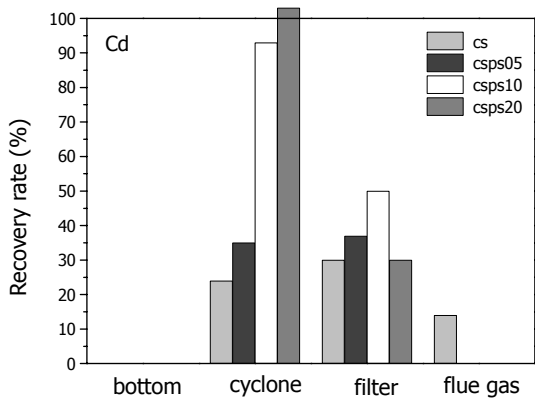


Figure 22e

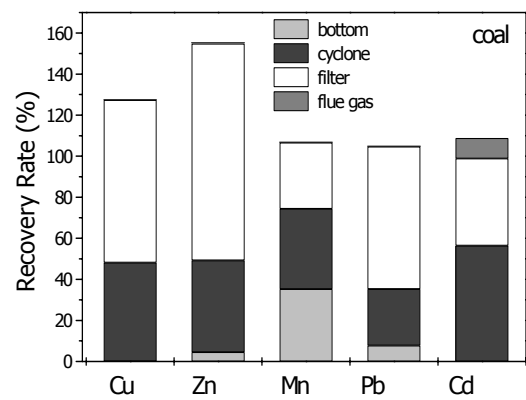


Figure 22f

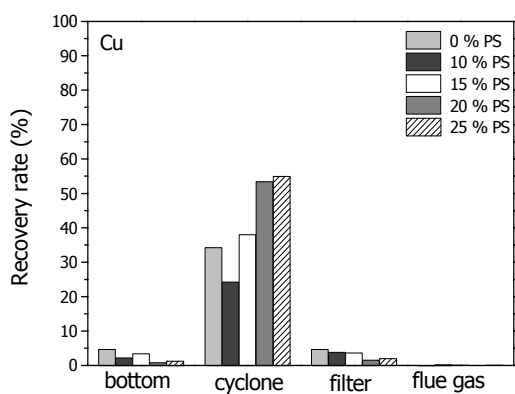


Figure 23a

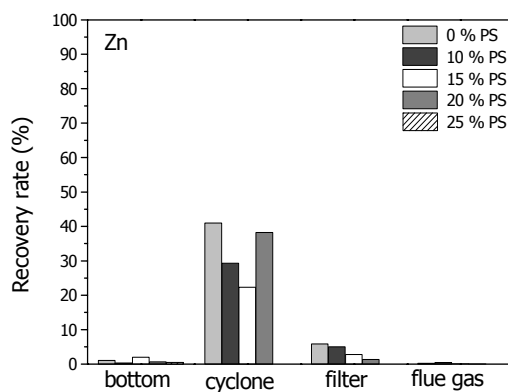


Figure 23b

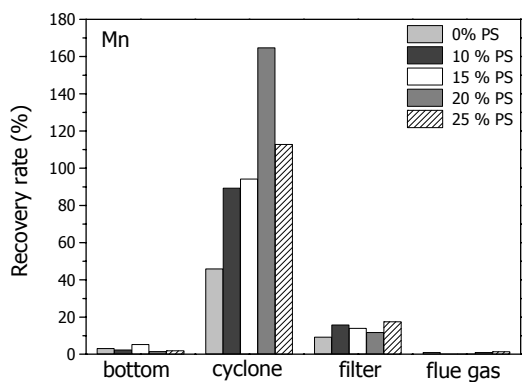


Figure 23 c

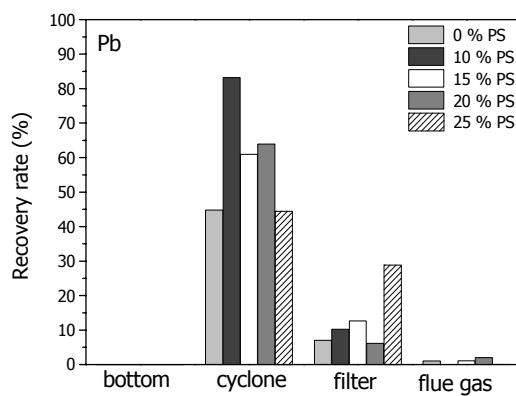


Figure 23d

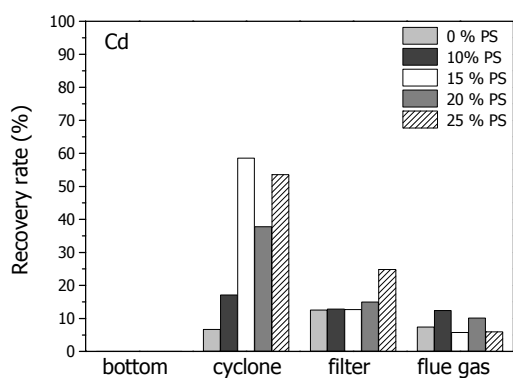


Figure 23e

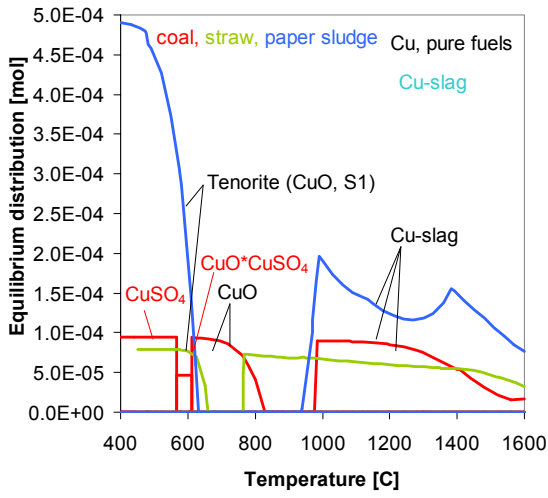


Figure 24a

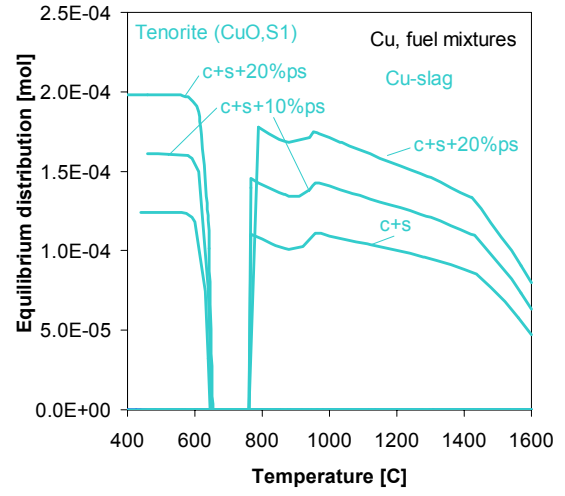


Figure 24b

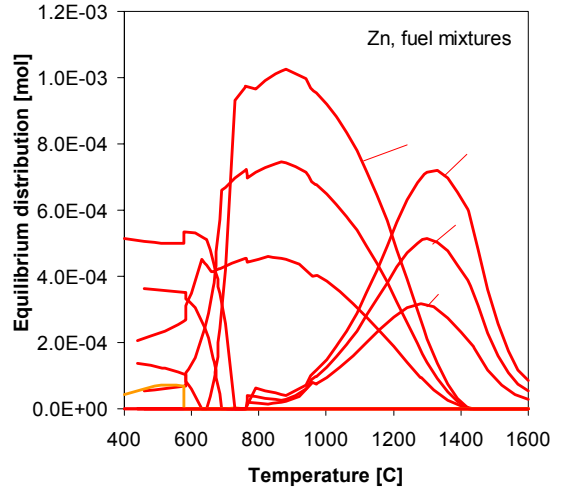
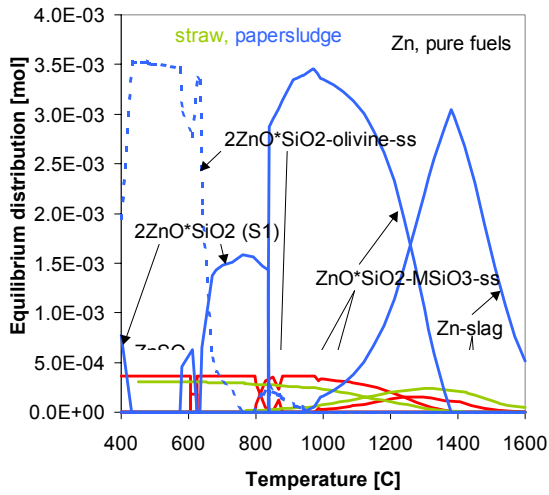


Figure 24d

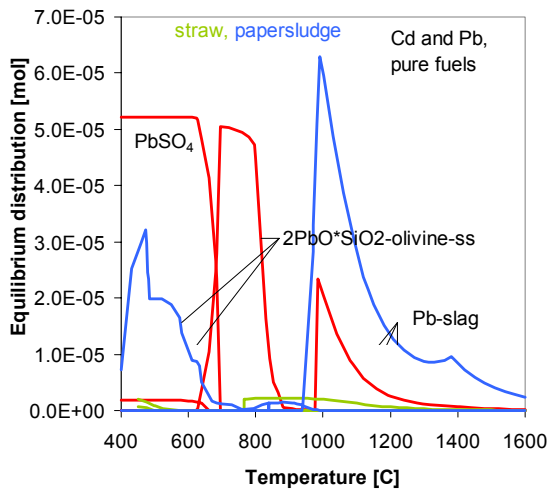


Figure 24e

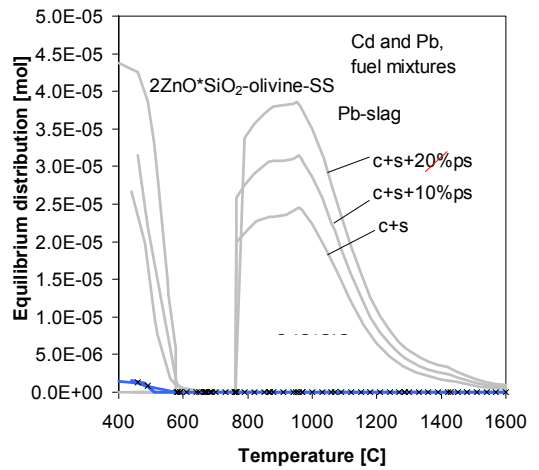


Figure 24 f

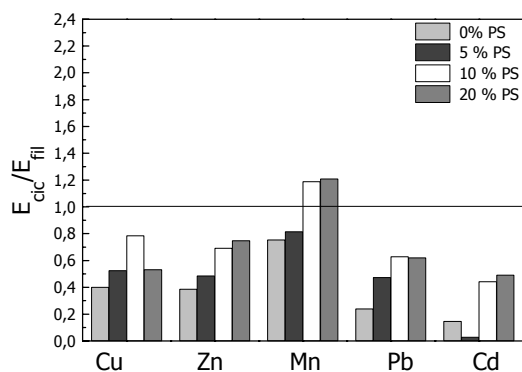


Figure 25a : Enrichment factor E_{cic}/E_{fil} for coal/straw/paper sludge blends. BFB mode.

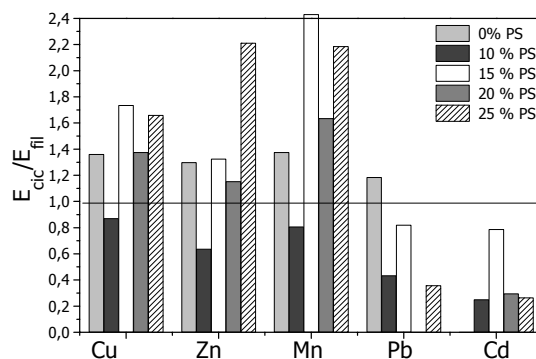


Figure 25b : Enrichment factor E_{cic}/E_{fil} for coal/straw/paper sludge blends. CFB mode

6.8.1 Behaviour of trace metals upon coal combustion

Ni –Cr. Ni amount in the flue gas was negligible (0,85%⁴); Cr was not detected under gas phase mode. Equilibrium calculations (not reported here) indicate that Ni and Cr are condensed at the conditions of the cyclone at 500 °C. Ni and Cr form condensed phases (respectively NiSO₄, Cr₂O₃) along the temperature range 400-900°C.

Pb. Experimental results show that Pb is captured to a small extent in the bottom bed upon coal combustion (3%). High share of Pb was found in the fine ash fraction, while the vaporised fraction of Pb in the flue gas is low (0,455 %). The equilibrium analysis shows that at 880°C, Pb exists in gaseous phases as Pb(g). The first solid condensed phase for the coal system is formed at about 800 °C. The formation of PbSO₄ begins at about 700° C, and at 500°C the amount of gaseous Pb would be negligible from the emission point of view. The formation of condensed phases for coal system begins at higher temperatures with respect to the paper sludge system.

Cd. Experimental results show that Cd is depleted in the bottom ash, indicating a total devolatilisation at bed temperatures. Equilibrium predictions are consistent with the experimental findings: at bed temperatures (800-880°C) no condensed phase is formed. Cd is mostly recovered in the fly ash streams, and a high share is found in the coarse fraction. Equilibrium calculations report that, for the coal system, Cd condenses as CdSO₄ at about 650 °C, and at 500°C condensation is completed. The Cd fraction measured experimentally at the stack is about 10%.

⁴ In this section, the numbers in brackets, where not specified, indicate the weight percentage of the element recovered in a specific mass output stream.

Cu The closure of the mass balance for Cu in the case of coal firing is reasonable good. The amount of Cu emitted in the flue gas is low (0,45 %) for coal combustion; the fraction of Cu found in the bed is also negligible. For the coal system, formation of the first condensed phases ($\text{CuO} \cdot \text{CuSO}_4$) begins at 820 °C, and at 400 °C the dominant specie is solid CuSO_4 , with negligible fraction existing in gaseous phase. The condensation for Cu in the coal system occurs in a higher temperature range with respect to the paper sludge system.

Zn. The behaviour of Zn is not easily interpreted due to the simultaneous presence of Zn in many different stable condensed phases over a wide temperature range. In the case of coal combustion, the amount of Zn recovered in the bed is about 5 %. Zn forms only condensed phases only in the temperature range 1000-400 °C ; at 880°C, Zn is predicted to be in the form of a Zn-silicate. The fraction measured after the stack is 0,7%, consistently with the low vaporisation indicated by the equilibrium calculations at those temperatures.

Mn The mass balance closure for the case of coal firing is relative good. Mn is equally distributed between coarse and fine fly ash; a relevant fraction is also found in the bed.

The above-described analysis has been referred to the BFB fluidisation mode. The correspondings results for CFB conditions will be analysed in the section for the coal-based blends.

6.8.2 Behaviour of trace metals upon firing coal/paper sludge under CFB mode: short remarks

Table 5 reports the speciation of solid phases at 500 °C for the elements Cd-Cr-Ni-Cu-Zn for the coal system and coal/paper sludge 25% system, and at 880 °C for this co-firing case. The experimental enrichment trends show that, upon co-firing, Cu, Zn, Mn, Pb tend to be recovered in high-temperature locations of the facility. For Cu and Pb, equilibrium calculations predict that, upon co-firing, the formation of condensed species is shifted towards lower temperatures than upon combustion of coal. While for the coal system the condensed species are sulfate compounds, for coal/paper sludge systems the condensed species are silicates and oxides compounds. Although the enhanced volatility of the elements predicted by the thermodynamic calculations is not consistent with the experimental findings, the enhanced recovery in the coarse fly ash mode may be explained by the large ash surface area available for gas-to-particle conversion routes when co-firing paper sludge.

For Cd the equilibrium calculations predict the absence of any condensed phase when co-firing paper sludge; in consistence with the high tendency to volatility, experimental findings indicate very high Cd enrichment in the fine fly ash upon co-firing blends

	Coal	Coal-paper sludge 25%	
	500 °C	800 °C	500 °C
Cd	CdSO ₄ (S1) – 99.8%	Cd(OH) ₂ (g)-36.4% Cd(g)-31.3% CdCl ₂ (g)-18.1% CdO(g)-14.9%	CdCl ₂ (g)- 99.3 %
Cr	Cr ₂ O ₃ – 100 %	Cr ₂ O ₃ (s)- 98%	CrH ₂ O ₄ (g)-0.5% Cr ₂ O ₃ - 99.5%
Cu	CuSO ₄ (S1)- 100 %	CuCl(g)- 100%	CuO-98.9% CuCl(g)- 1.1%
Ni	NiSO ₄ (S1)-100%	Ni ₂ SiO ₄ - 99.6%	Ni ₂ SiO ₄ - 99.6%
Pb	PbSO ₄ (S1)-100%	PbCl ₂ (g)- 41 % PbO – 56%	PbCl ₂ (g)- 65.9 % PbO ??
Zn	ZnSO ₄ (S1)- 100%	ZnSiO ₃ - 99%	ZnCl ₂ (g)- 0.5% Zn ₂ (SiO ₄)- 99.3%

Table 5: Condensed phases of toxic trace metals for coal system and coal/paper sludge 25% system

6.8.3 Behaviour of trace metals upon firing coal/straw/paper sludge blends

Ni: The share of Ni detected in the flue gas upon coal/straw firing for BFB is 1,1; %. Ni was not detected under gaseous phase for the experiments under CFB conditions. Equilibrium calculations report that Ni forms only condensed phases under silicate form all the temperature

range 400-900°C.

Cr: Cr was not detected in the gas phase. Unlike Ni, Cr is condensing entirely at 650 °C as oxides. Therefore, low risk is expected associated to presence of these toxic metals in gaseous phase when co-firing.

Pb. Approximately 10% of Pb was found in the bottom ash when firing coal/straw (50%/50%) under BFB combustion mode. When adding paper sludge to coal/straw/blends, the portion of Pb recovered in the bottom ash increases. The vaporised fraction for coal/straw (50%/50%) is 0.23%. When co-firing paper sludge, enhancement of total recovery of Pb on fly ash is found. Addition of paper sludge leads also to an increase of the ratio E_{cic}/E_{fl} . Under CFB conditions, Pb is not recovered in the bottom bed ash; the share found under gaseous phase is decreasing, and this is consistent with the experimental enhanced recovery in the cyclone.

Differences of enrichment trends between CFB and BFB may be imputed to differences in particle size distribution; for CFB conditions the cyclone ash comprises finer particles than BFB. Equilibrium calculations correlate well with the experimental findings for BFB combustion mode, since Pb is predicted to dissolve partly into the melt at 880°C, whose amount increases as the share of paper sludge increases. The equilibrium predictions show that the formation of condensed phases begins at 650 °C when co-firing; at 500 °C the portion of Pb as $PbCl_2$ in gaseous form, decreases from 50% (coal/straw 50%/50%) to 18% (coal/straw/paper sludge 20%); this depletion in vaporisation is consistent with the experimental recovery enhancement in the ash streams observed under BFB and CFB conditions.

Cd For BFB conditions, high shares (13%) of Cd are measured in the flue gas for coal/straw (50%/50%). The mass balance closure for coal/straw firing is poor; however, total recovery is enhanced when co-firing. Cd was not recovered in the bottom ash, indicating a total devolatilisation at bed temperatures. Cd is highly enriched in the fine particle mode. The enrichment trends are similar for both CFB and BFB combustion mode, indicating an increase upon co-firing. The share of Cd in the flue gas for CFB firing conditions is also quite high (in the range 12-14%).

For the blends, formation of condensed phases- $CdO \cdot SiO_2$ -is predicted to begin at about 450 °C. Co-firing paper sludge leads to enhanced formation of vaporised compounds at low temperatures; at 500 °C the share of Cd in the flue gas (as $CdCl_2$) is increasing when increasing the share of paper sludge in the blend.

The high Cd volatility along a wide temperature range, predicted by equilibrium calculations, is consistent with experimental findings, indicating a very high enrichment in the fine fly ash mode.

Cu Cu recovery is reasonable good for the blend coal/straw (50%/50%), and 1.23 % is emitted

as flue gas. The experimental partitioning for BFB combustion show that the amount of Cu recovered in the bed is increasing at higher shares of paper sludge fired. This occurs in correspondence of higher melting amount. Cu is enriched in the fine and coarse ash fraction when co-firing; the ratio $E_{\text{cic}}/E_{\text{fil}}$ is increasing when the share of paper sludge in the fuel blend is higher. For CFB conditions, Cu is slightly depleted in the bottom ash, while the recovery in the coarse fly ash mode is slightly increasing when co-firing. Cu fraction found in the flue gas is decreasing. Similarly to the trends shown under BFB firing, the enrichment trends for CFB firing conditions show a depletion of enrichment in the fly ash upon co-firing.

Consistently with the experimental data obtained under BFB conditions, equilibrium calculations show that when burning coal/straw/paper sludge blends, Cu is dissolved in the melt forming at bed temperatures. No significant additional impact of paper sludge addition on Cu behaviour is predicted by the equilibrium calculations. The melt is occurring to a less extent for CFB combustion than for BFB combustion. The melt is forming but there is little experimental evidence of retention of Cu in the melt. According to equilibrium calculations, at 700 °C condensed phases begin to form, and at 500 °C the amount of Cu in the gaseous phase is negligible. Formation of tenorite is predicted to begin at temperatures around 650° C.

Zn Experimental results show that upon combustion of the coal/straw blend (50%/50%) at BFB conditions, Zn is depleted from the bed (2%); 0.25 % of Zn was found in the flue gas. For the blends including paper sludge, very low bed retention has been also observed, independently of paper sludge addition. The share of Zn found in the coarse ash fraction is higher when firing higher shares of paper sludge. The increasing trend for the variable $E_{\text{cic}}/E_{\text{fil}}$ calculated for BFB conditions is consistent with the enhanced capture in the coarse fly ash when co-firing.

For CFB conditions, Zn is slightly depleted in the bed; with its retention is less than 5%. Low closure of the mass balance is observed. Zn is mostly recovered in the cyclone ash. The variable $E_{\text{cic}}/E_{\text{fil}}$ indicates a higher depletion in the filter ash upon co-firing. Zn share in the flue gas is negligible when firing paper sludge blends.

The comparison of equilibrium calculations and mass partitioning data is difficult due to the presence of several condensed phases. In contrast to the experimental findings, indicating depletion in the bottom ash, equilibrium calculations show that Zn is present at bed temperatures (880°C) almost entirely in the form of a silicate solid solution, suggesting that a higher retention in the bed should occur. At temperatures between 620°C and 700°C, a silicate phase is formed, and at 600 °C for the case of 10% and 20% paper sludge an olivine phase co-exists. Formation of $\text{ZnO} \cdot \text{SiO}_2$ will occur at higher temperatures when adding paper sludge in the blend.

At 500 °C, negligible Zn gaseous amount for all the fuel blends is predicted to form. The

decrease of enrichment in the fly ash is consistent with the enhancement of formation of condensed phases at higher temperatures.

Mn Upon combustion of coal/straw/paper sludge blends for BFB conditions, a slight Mn depletion in the bed is found. No significant impact of paper sludge addition on the recovery in the fly ash and on the mass partitioning was observed. The variable $E_{\text{cic}}/E_{\text{fil}}$ is increasing in correspondence of paper sludge co-firing. For CFB conditions the variable $E_{\text{cic}}/E_{\text{fil}}$ is not markedly dependent on the share of paper sludge in the blend. The results generally display a negligible impact of paper sludge addition on Mn behaviour, and a tendency for Mn to be captured in coarse fly ash.

6.8.4 Discussion of the results

In comparison to the paper sludge system, condensation of vaporised trace metals for coal system is occurring generally at higher temperatures. It is important to note that for the coal system, sulphates are the dominating species in which the trace metals are bound, while for the paper sludge system the formation of silicate-based phases is prevailing. Particle size distribution of fly ash formed upon combustion of coal is different than upon combustion of paper sludge.

These remarks are important because, upon replacement of coal with paper sludge, the shift in the phases observed for the single fuels is going to occur also for the fuel blends.

Equilibrium calculations, in agreement with experimental data on bed agglomeration tendencies, indicate the increase of ash melting amount at typical bed temperatures (880°C) when increasing the share of paper sludge in the blends (Sandelin et al, 2001). It was also shown that Cu, Zn, and Pb are dissolved in the slag. Upon co-combustion, a higher recovery in the bottom ash for these elements was found; the recovery is higher under BFB mode, where the melt occurred to a higher extent, while under CFB mode the melt formation process is less pronounced.

Equilibrium calculations show that for fuel blends, Cu, Zn, and Pb form condensed phases at temperatures between 600°C-700°C; silicates compounds are prevailing. The increase of the ratio $E_{\text{cic}}/E_{\text{fil}}$, observed when firing higher share of paper sludge in the fuel blend, indicates an enhanced metal capture on the coarse fly ash fraction, consequently reducing the share of trace metals which could condense on fine fly ash fraction along the flue gas path. The enhanced capture of the metals on the coarse ash fraction upon co-firing may be related to the large generation of ash particles with particle diameter <10 µm, leading to large surface area available for trace metal capture. This phenomenon is related to the ash structure, and to the formation of fly ash agglomerates. The availability of particle with large surface area results effective in binding the toxic metals onto the coarse recovered fraction hindering their condensation and their

subsequent enrichment in the finer ash fraction.

If only physical condensation would occur, this would drive vapours towards lower size particles, due to the higher surface area, and the parameter $E_{\text{cic}}/E_{\text{fil}}$ would consequently decrease. If the parameter $E_{\text{cic}}/E_{\text{fil}}$ increases, it may be suggested that chemical reaction paths will be dominant.

For Cd and Pb, an enhancement of total recovery in the fly ash was observed. As reported in chapter 2, studies have demonstrated the existence of scavenging reactions of Pb and Cd from kaolinite and lime, on particles finer than 10 μm . These two compounds are present in the sludge ash.

Indirect information on the speciation of the elements come from the equilibrium calculations, which show that Cu, Zn, Pb, Cd, are bounded to silicates in the fly ash. Therefore, with respect to environmental impact, not severe consequences as when the metals are water-soluble are expected.

Risk may be associated, however, to the very high Cd enrichment observed for the fine fly ash. Equilibrium calculations predict that the impact of paper sludge addition is to enhance vaporisation and to increase the share of gaseous Cd as CdCl_2 in gaseous phases. Condensation of CdCl_2 on fine particulate, occurring simultaneously with the condensation of alkali chlorides at filter temperatures, might be a reason for the high Cd enrichment in the fine fly ash.

The variable $E_{\text{cic}}/E_{\text{fil}}$, giving a qualitative indication of the propensity of a metal to be enriched in the ash fraction, displays similar trends with respect to paper sludge addition for Cu, Zn, Mn, Cd. Only Pb is an exception. It is evident that for Cd phenomena of physical condensation on fine particulate will prevail, while for the other metals it is suggested that chemical reactions play an important role for their capture.

7. CO FIRING PAPER SLUDGE IN LARGE-SCALE BOILERS: TRANSFERABILITY OF THE RESULTS

This chapter deals with the analysis of a measurement campaign carried out at large-scale facility (LSF), from which the validation of the lab-scale results can be assessed. Some general conclusions for the transferability of the TSF results will be drawn.

7.1 Comparison of the test-scale experiments with the co-firing test runs effected at Midkraft power plant (80 MWth)

In this section a short presentation of the results of an experimental campaign of co-firing of paper sludge with coal and coal/straw will be given. The experimental campaign was performed at the 80 MWth CFB boiler of the Midkraft Power Company, located in Grenå, Denmark. Coal, paper sludge and straw used in this campaign were supplied for the corresponding tests in the TSF. The utilisation of the same fuels is of great added value for the comparison between the 2 facilities. The maximal share of paper sludge fired in the LSF was 12,5 % on an energy basis. The results presented in this section are covered to a larger extent in the final report of the project JO3R-CT97-0191 (Aho et al, 2001). The purpose of the comparison was to ascertain the

prediction capability of the small-scale boilers. Focus of the study is the ash behaviour.

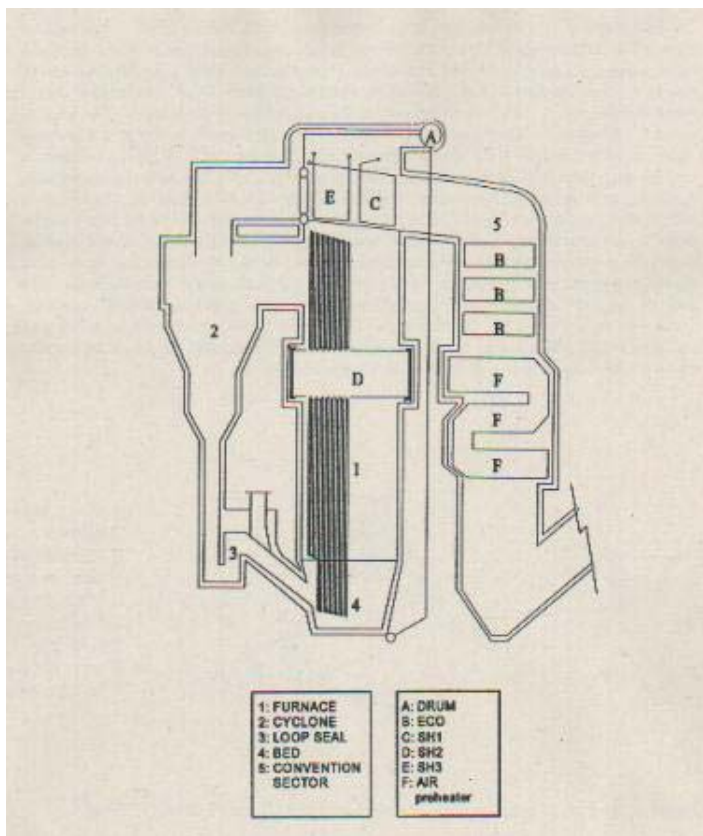


Figure 1: Schema of Midkraft 80 MWth boiler

7.1.1 Description of the plant and of the test campaign

The schema of the plant is shown in **Figure 1**. The boiler of the co-generation plant is an Ahlström Pyroflow designed for 0-60% straw and 40-100% coal on an energy basis. The plant has a thermal output of 50 MJ/s (district heating and process steam) and an electric capacity of

17 MW. The fuel mixture is fed into the boiler, where it is burned at relatively low and uniform temperature in the range 800-920 °C. The bed material and the unburned particles are separated from the flue gas in two parallel cyclones and recirculated through a loop seal to the bottom of the combustion chamber.

The figure shows also the schema of the superheater sections. Fly ash was sampled at the Electrostatic precipitator (ESP), not shown in the picture. Aerosol measurements were effected at the entrance and at the exit of the ESP, at a temperature of 125 °C. Aerosol measurements were effected by means of a Berner multi-jet Low Pressure Impactor (LPI); details of sampling techniques and sampling characterisation are reported in literature (Aho et al, 2001).

Fly ash coming from a stoker-fired was used as additional bed material during the test runs in the LSF. This fly ash contains more than 40% wt. of unburned carbon. As it will be reported later on, the presence of additional bed material in the LSF impacts the ash elements partitioning and ash composition, and it is one reason for the differences existing with the trends observed in the TSF. The presence of a large char amount in the bed section impacts also the behaviour of gaseous polluting emissions, especially $\text{NO}_x/\text{N}_2\text{O}$.

In the TSF, the fly ash is separated in two streams; the first, coarser fraction, comes out from a cyclone operating at 350-400 °C; the second, finer fraction, is separated in a ceramic candle filter, kept heated at a mean temperature of 150 °C. In the LSF, on the contrary, the ash particles are removed in three separated streams corresponding to the three zones (Z1, Z2, Z3) of the ESP, at a uniform mean temperature range of 120-130 °C. Due to the differences of the temperature-time histories of the two gas/particles flows, the ash-output streams characteristics will differ in terms of ash composition and particle size distribution.

Previous test runs (Hansen, K.W., 1999) had shown that the mean ash particle size of the ESP's zones Z1-Z2 was in the range 12-6 μm , for coal firing, and 6-15 μm for coal/straw (50%/50%) firing. These results are very similar to particle size distribution for the fine fly ash fraction recovered at the filter of the TSF. Z3 particle size distribution was not known, but it is supposed to have a finer particle distribution.

An exact comparison of the combustion behaviour in the TSF and LSF is, therefore, prevented by dissimilarities concerning both hydrodynamics and combustion chemistry. Three-dimensional effects in large-scale boilers are also not relevant in the TSF.

Under this restriction, the following analysis aims to ascertain qualitatively the impact of paper sludge upon co-firing, and to assess whether similarities between the two plants occur with respect to ash behaviour. In a later section, hydrodynamic and combustion scaling-up laws will be discussed.

The following table reports the blend mixtures that were burned at the industrial-scale boiler (percentage on an energy basis):

Coal (%)	Straw (%)	Paper sludge (%)	Blend nomenclature
100	0	0	100/0/0
90	0	10	90/0/10
48	52	0	48/52/0
43	46	12	43/46/12

Table 1: Composition of the blend burned during the test runs at the LSF – with corresponding nomenclature.

7.1.2 Emissions Trends

Large fluctuations were recorded for SO₂ trends at the LSF; these were depending on the fluctuations of the limestone inputs, so that no clear dependence of the fuel mixture could be found. In the TSF, on reverse to the LSF, SO₂ emissions decreased when co-firing paper sludge, due to the higher amount of available alkali enhances the sulphur recovery in the fly ash. As far as HCl concerns, the results of the two facilities are in a general good agreement, showing that HCl emissions increase when introducing straw in the fuel mixture. Similarly, adding paper sludge increased in both cases HCl emissions when firing coal-based mixtures, while a decrease of the emissions was observed upon combustion of coal/straw based blends (Aho et al, 2001)

7.1.3 Main ash-forming constituents

An enrichment factor has been introduced to analyse the ash behaviour for the LSF (Hansen, K.W., 1999). This factor relates the composition of ash-output streams to the coal ash composition. A similar factor has been introduced for the fine fly ash (filter) sampled during the corresponding experiments at the TSF under CFB mode. **Figure 2a** shows the values of the enrichment factor vs. the paper sludge share in the fuel blends for the TSF, while **Figure 2b** reports the values for zone 2 at the ESP of the large-scale unit. As a result of high potassium concentrations, the filter ash is extremely enriched in K for coal-straw fired mixtures. The two series of test runs display comparable results with respect to the behaviour of K and Cl. The enrichment trends exhibit higher values in the filter ash for coal-straw based mixtures. Na

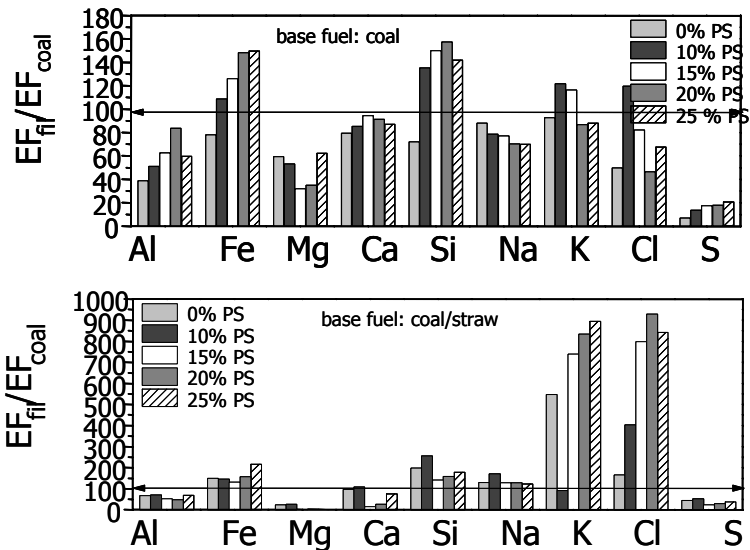


Figure 2a: Enrichment factor calculated for filter ash of the TSF under CFB mode. Basis is the coal ash composition

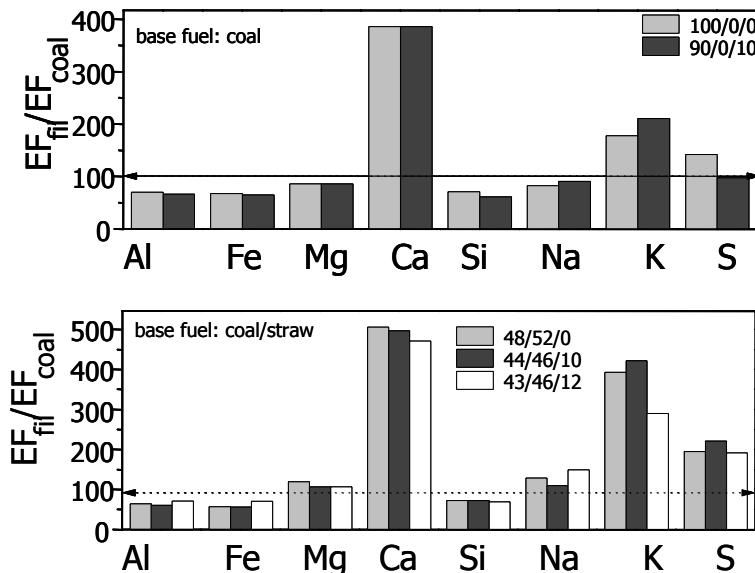


Figure 2b: Enrichment factor calculated for the zone 2- Z2- of the ESP for the LSF. Basis is the coal ash composition

enrichment is also increasing, when adding paper sludge to the coal-straw blends. This was also observed during the large-scale boiler test runs. In chapter 6 it had been reported that the water-soluble concentration of K and Na is increasing for coal/straw –based blends at the TSF, but a less clear impact of paper sludge addition was found for the LSB. The water-soluble fraction of alkali is higher for the fine ash mode (Zone II), in analogy to what was observed at the TSF. Similar analogies were found with respect to Cl concentration, which was higher in the fine fly ash when firing coal/straw-based blends.

In both cases, a generic trend of Al depletion is observed. For the TSF, Fe has a higher enrichment in the filter; the recovery is also increasing at higher shares of paper sludge. The enrichment factor value for Si is also very high, and this is due to the fragmentation of sand particles reaching the separators devices of the facilities.

While the trends for K, Cl, Na are quite in agreement, it is difficult at this stage to describe the discrepancies or analogies of behaviour for the other elements. This is mainly due to the variation of parameters, like the different amount of additives and different bed ash used for the test runs.

7.1.4 Trace elements

The concentrations of the toxic trace metals Cu-Cd-Zn-Pb in the various ash output streams of the two facilities have been compared. The values are plotted in **Figure 3a-3d** for the TSF scale facility and **Figure 4** for the LSF.

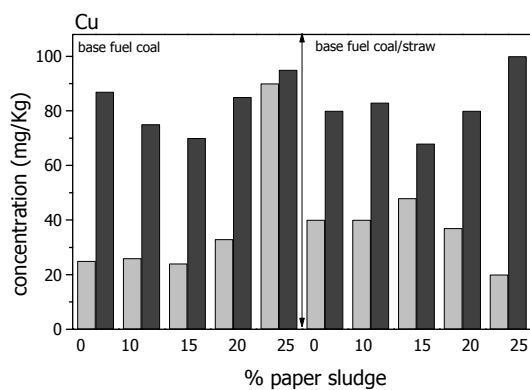


Figure 3a

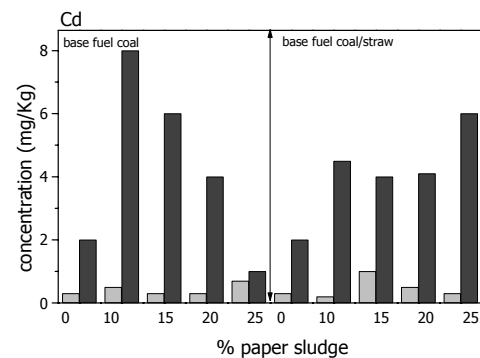


Figure 3b

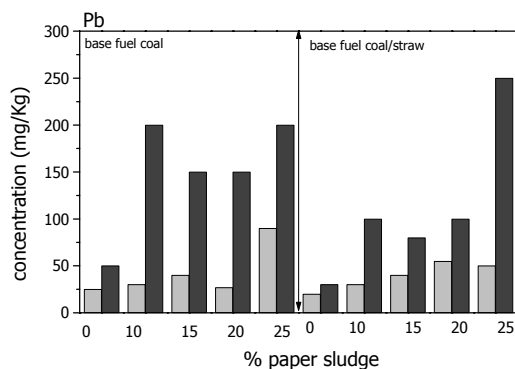


Figure 3c

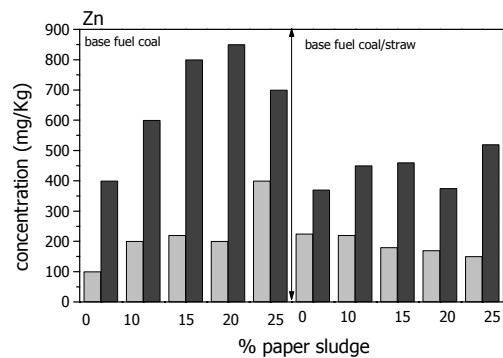


Figure 3a-3d: Concentrations of trace metals in CFB cyclone ash (light gray) and filter ash (dark grey). X variable represents the share of paper sludge in the blend.

Cu: Cu concentrations in the fly ashes increase shifting from coarser to finer particles. This tendency is observed for both TSF and LSF. A general increase of the concentrations is observed when firing paper sludge for coal-based blends. The impact of paper sludge addition for coal-straw based blends is, on reverse, not clear. It must be considered that large differences were found for Cu content in paper sludge and in the coal when performing Round-Robin tests for the fuels (chapter 6).

Cd: Cd concentrations range is very similar in the different ash streams. High enrichment in the finer particle size range is observed at TSF and LSF.

Pb: At the TSF, Pb concentrations in the fine ash particles are much higher than in the coarse. A similar behaviour is observed for the LSF. Increase of Pb concentrations in the fly ash is found at higher shares of paper sludge in the blends.

Zn : At the LSF, for coal-based blends, tendency for Zn enrichment in the small particles was observed, while for coal/straw/paper sludge blends concentrations are lower. However, paper sludge addition in the blends provokes an increase in the enrichment in fine particle mode. These data are in a very good agreement with the corresponding results obtained at the TSF, where the enrichment for the fine particle mode has been observed to be much higher for coal blends than for coal/straw-based blends.

Mn: At the LSF, upon combustion of coal/straw/paper sludge blends, Mn is highly enriched in the smallest particles, the enrichment being higher than upon combustion of coal-based blends. A dissimilar behaviour was observed for the test-runs at the TSF, where no significant enrichment of Mn in the small fly ash in the case of coal/straw/paper sludge was observed (figures not reported here).

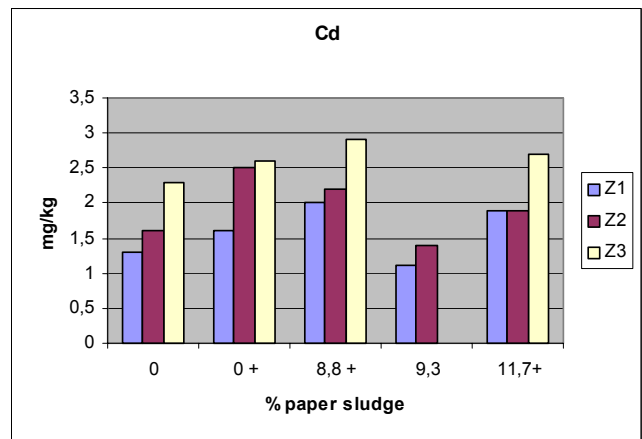
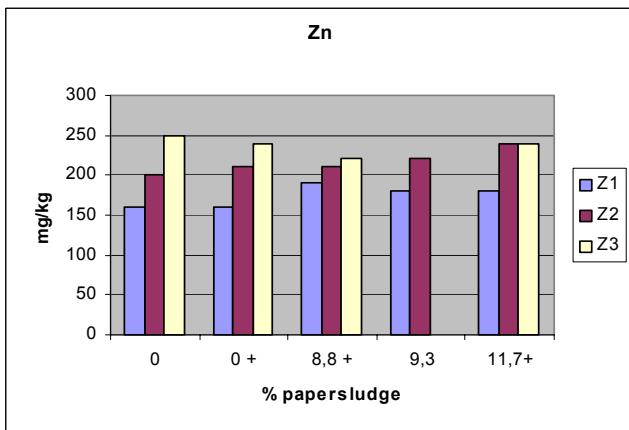
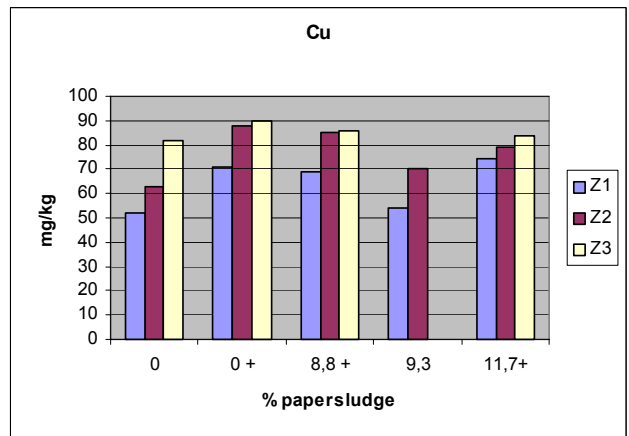
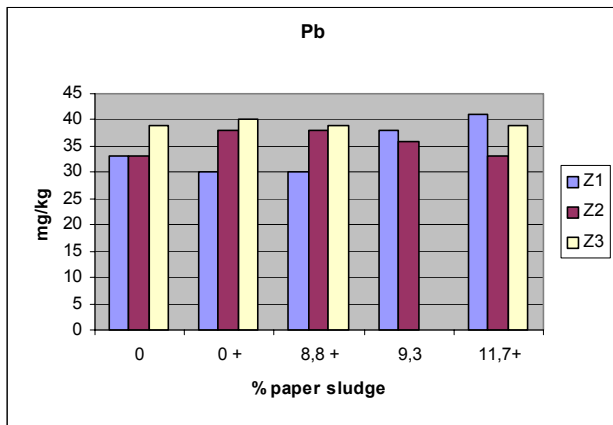


Figure 4a-4d. Concentrations of trace metals at the ESP of the LSF. Zone 1, 2, 3(Z1-Z2-Z3). Coal/paper sludge and coal/straw/paper sludge blends. (The X variable represents the share of paper sludge in the blend; the symbol + indicates the presence of straw in the blend, the Y variable the concentration of the trace metals in the fly ash). Figure reported from literature (Hansen, K.W., 1999).

7.1.5 Discussion

Some important factors must be taken into account to compare the test runs at the LSF with the results at the TSF.

- The discontinuous utilisation of a fly ash stream used as an additional bed material in the LSF facility;
- The lack of long-term duration of steady state experimental conditions due to fluctuations in the additive (limestone) dosage and in the fuel dosage, leading to fluctuations in the temperature and gaseous emissions profiles of the LSF facility;
- The different separators device, which corresponds to a variation in the temperature/time history for the fly ash in the two facilities.

The comparison has been restricted to assess qualitatively the impact of paper sludge addition on ash behaviour for the two fuel blends. The analysis is confined to the partitioning of the main-ash forming constituents and the concentrations of the toxic trace metals in the different fly ash streams.

The relatively short duration time of the test runs at the LSF facility prevented the system to get into equilibrium (Hansen, K.W., 1999). Therefore, as the “previous test run” impact cannot be avoided, it results difficult to assess whether and how this influences the partitioning of the trace metals in the ash streams.

For both the two systems, shifting from coal to coal-straw blends caused large differences of fly ash composition; however, the impact of paper sludge addition is not so evident for the LSF boiler.

Similarities were found with respect to alkali enrichment and alkali water-soluble fraction for fly ash when firing coal/straw based blends. Results concerning the partitioning of Cl in fly ash and flue gas were in agreement, too.

With respect to trace elements concentrations in the fly ash streams, good agreement was found for Pb and for Zn enrichment in the fine fly ash. The differences concerning Cu, Mn and Cd, on the contrary, are at this stage difficult to be explained in detail.

7.2 Transferability of the results in an industrial-scale boiler

The results of the study raise the following question: to which extent are the results and the study of the ash behaviour from test-scale FB boilers transferable to commercial-scale combustors.

Factors that may influence the behaviour of the ash-forming constituents in combustion systems are:

- The thermal behaviour of the reactor – defining the temperature/time history of the combustor
- Particle temperature
- Particle entrainment/ash partitioning
- Reactions with materials
- Aerosol dynamics/condensation behaviour
- Particle capture devices

Technical factors affecting the scaling-up of the results include generally:

- Combustor design
- The temperature/time history of the flue gas cooling path

Some of these topics will be tackled in the following section

7.2.1 Combustion chamber: scale-up analysis

So far, scale-up analysis of fluidised bed combustors has been concentrated mostly on the fluid dynamics of the fluidised bed. Empirical work has been performed on the effect of parameters like bed height, particle size, etc. Classical criteria for hydrodynamic scaling-up keep constant a series of adimensional parameters (Knoebig et al, 1998):

- Re_1 (the Reynolds numbers based on the characteristic length of the fluidised bed);
- Re_2 , (the Reynolds numbers based on the particle diameter),
- Fr , (the Froude number based on a characteristic length of the bed)
- the dimensionless net flux of solids, (especially in the case of CFB boilers).

General good agreement with respect to the axial solid distribution in a full-scale combustor and small-scale combustor has been achieved when a proper set of adimensional parameters has been respected (Knoebig et al, 1998).

One scaling criterion for the fluid dynamics of two different reactors may be the choice of a similar gas residence time:

$$(H_I/u_I)=(H_{II}/u_{II})$$

(H= height; u= gas velocity, I, II: first and second reactor)

which yields a relation between the fluidisation velocities and the height of the combustion reactor. Also the average solid concentration (solid hold-up), that determines similar relationships concerning the pressure drops between the two facilities, may be a very important factor.

Recently, the importance of a correct scale-up for both fluid dynamics and combustion kinetics has been pointed out, as hydro dynamical similarities may not be sufficient to allow the transfer of results from small-scale combustion experiments to a large boiler (Leckner et al, 2000). This makes difficult the fulfilling of both types of criteria. Important macroscopic parameters that should be kept identical to compare large and small-scale facilities are bed temperature, total excess-air-ratio, primary stoichiometry, fuel, and bed material. It is also preferable if the fluidisation velocity is also in the same order of magnitude as in the full-scale plant.

The “hydrodynamic” scaling-up needs to be comprised with a scaling-up of the combustion reactions. One criterion to determine the height of the riser is the time needed for a relevant gas-phase reaction, i.e., the carbon-oxygen combustion reaction (Knoebig et al (1999).

In this study, the gas reaction time of the TSF was in the usual range of BFB large-scale operation (about 5-6 seconds), and the fluidisation velocity (0,6-0,7 m/sec) was in the same range, too (the usual gas velocity for stationary FBC is in the range of 1,2 m/s, Anthony et al, 1995b; Leckner, 1998). The temperature profiles in the riser of the TSF were also within the range of the usual operation at FB boilers. Quartz sand was used as a bed material, a very typical material for FB boilers. Air-staging similarities with an industrial FB boiler could be also easily achieved. The solid hold-up was also quite similar in the case of same bed material. The goal of maintaining the set of macroscopic similar combustion conditions was therefore achieved.

Considering the TSF under CFB conditions to industrial-scale boilers, the residence time in the riser should be slightly higher to reach the similar conditions as in a large-scale boiler.

Leckner et al. (2001), have suggested a semi-empirical criterion for a scale-up on the horizontal direction of the plant. This is based on the Damkholer number, Da , related to combustion reactions (devolatilisation and char combustion), by distinguishing high-volatile fuels for which devolatilisation plays a dominant role, and coal, for which char combustion is dominating. In order to have a good degree of mixing between the different combustion reagents, the following condition must be fulfilled:

$$Da < 1$$

With $Da = \text{transport time}/\text{reaction time}$.

This parameter gives a qualitative estimation of the degree of mixing between the fuel and the fluidisation air, which are usually supplied at different points. It can be assumed that for $Da < 1$, the mixing will be good enough, and prevailing excess of oxygen, even locally, is expected.

For high volatile fuels the following equation is can be used:

$$(x/1000d) \leq 0,14$$

while with char as a fuel

$$(x/1000d) \leq 1,4$$

where x is a characteristic horizontal dimension of the combustion chamber, and d the fuel particle characteristic diameter, as fed to the bed .

The condition $Da < 1$ is fulfilled by the TSF, and it is valid for both volatile fuels and coal, in both fluidisation modes.

Generally in test-scale reactors, the mixing rate of the fuel and air is good, and oxidising conditions are therefore uniformly prevailing through all the combustion chamber; a different situation occurs in a large-scale boiler. In dependence of the mixing degree, the conditions in the bottom part of a circulating bed reactor may be mostly reducing. A fraction of the fluidising air bypasses the bottom bed with high velocity, thus not mixing completely with the gas, until the upper part of the furnace. In the bottom part of the furnace, the gas concentration may periodically change between oxidising and reducing; in the upper part of the furnace and in the re-circulating cyclone, the conditions will be mostly oxidising; upon combustion of biomass fuels for which long devolatilisation and drying times occur, the re-circulating cyclone is the region where the burnout of the char occurs to a large extent (Leckner, 1998). In these regions the gas temperature may exceed the bottom temperature of more than 200 K. The conditions of a test-scale facility and a large-scale boiler tend to become more similar in the upper region of the reactor (Leckner et al, 2001).

If scale-up issues concerning the behaviour of the main polluting emissions have been recently subject of investigations, less work has been done on the scale-up of ash-related phenomena. The occurrence of reducing conditions at the bottom of a large-scale combustion reactor, not prevailing in a test-scale facility, may lead to a decrease of the particle temperature, thus influencing the volatilisation of the ash-forming elements (Quann et al., 1982). Because of differences in particle temperatures, consequences on the behaviour of the ash melting, bed agglomeration in the bed, and on the devolatilisation of the ash-forming constituents are expected.

7.2.2 Influence of the particle removal system on trace metals capture

The particle-bounded trace metals are separated according to the specific flue gas cleaning technology. Generally, fabric-filters remove particles impinging them upon the filter material, due to impaction, interception, electrostatic attraction and diffusion, in dependence mostly on the particle size. An ESP collects particles by generating an electrical charge on the particles, which

will be later collected on a surface having the opposite charge. Generally the removal of the fly ashes does not tackle the total particle-size spectrum. The very small particles (less than 1 μm), on which usually the trace elements are enriched, are not successfully removed and they are emitted to the atmosphere. The capturing efficiency of these devices is dependent on the particle size, density, composition, and other process parameters like temperatures, moisture content and gas loading.

The removal of the trace metals may be also dependent on the temperature/time history of the flue gas cooling section. It may happen that, if the particle-removal system operates at temperatures as high as 350 °C (like a hot-side ESP), the gas-forming trace metals are not completely condensed and they will pass the ash-removal facility. At lower temperatures -130-150°C- (cold-side ESP), condensation of volatile trace metals is completed. The condensation of elements like As, Hg, Se may not be completed even at such low temperatures.

Most of the baghouse filters and ESPs work at efficiencies of 99,9 % or more, but they have a very low efficiency for the range 0.1-1 μm particles. Especially ESPs have low capture efficiency for ultrafine particles, as smaller particles are difficult to charge to a sufficient level for electrostatic collection. Smith et al. (2000) indicated that ESPs have a capture efficiency lower than 99% for Sb, Be, P, Ni, Hg, Mo. Meji reports a capture efficiency lower than 99% for Sb, Cd, Se, Pb, Zn (Meij, 1989a). Other works (Tumati et al., 1991) indicate that As and Cd are strongly enriched in the finer particulate at the exit of the ESP and elements like Sn, Sb, Pb, Ni are instead moderately enriched.

Although baghouse filters are often considered superior to ESP for the capture of fine particles, and should have higher collection efficiencies for the associated trace metals, they may have problems with the on-line cleaning systems due to the re-dispersion of collected particulate. The continual presence of fly ash and residual carbon on the baghouse filter surface can help to trap more volatile trace elements. The ash layer might adsorb these components.

The examples reported above concern only the toxic trace metals, but similar observations are valid for all the species that may exhibit a high volatility upon combustion (sulfates, chlorides, etc).

It is out of the scope of this work to initiate a detailed theoretical study for the scale-up of the flue gas cooling path section. Few data have been so far published upon the effectiveness of test-scale facilities to predict the behaviour of the trace metals upon combustion and upon cooling. In particular, work on the FB combustion technology is so far limited. In the EU-funded project

JOR3-CT97-0191, on whose framework the present doctoral thesis has been done, a number of attempts have been made to compare the chemical composition of fly ash samples from small and large-scale facilities running under similar conditions in terms of operative parameters (fuel, residence time, air staging, etc). The results have shown generally a high similarity in the ash composition of the main constituents, independently on the scale of the plant or the combustion mode. This finding supports the theory that, when macroscopic combustion and hydrodynamic scale-up criteria are fulfilled (like gas total residence time, temperature profiles, air-staging, fuel, etc), similar flue gas and fly ash composition are obtained.

A comparison concerning the partitioning of the trace metals when burning coal/sewage sludge blends in the TSF and an industrial-scale boiler (12 MWth) has been reported in detail (Åmand et al, 2001). The results showed that the distribution of elements like Cu, Cd, Mn, Pb between bed, coarse and fine fly ash was similar.

Differences of distribution were relevant for Hg and Cd: the temperature of the separation devices, as well as different particle loading, played a major role. A separation device operating at 150 °C captures Hg, whereas a device operating at 350 °C does not perform well in this respect.

7.2.3 Gas-to-particle conversion routes in the flue gas cooling section

Another important scale-up issue concerns the simulation of the temperature/time history of the post-combustion zone of the flue gas channel, where the gas-to-particle conversion routes take place.

As previously discussed, the enrichment of the toxic trace metals into the fine particles derives either from heterogeneous condensation, coagulation, or chemical reactions. The fraction of the toxic metals that can condense is depending on the partial pressure of the metal and on the saturation pressure (Martel, 2001). The temperature influences indirectly the process (dependence on the saturation pressure). In addition, it governs also the kinetic of the process. Heterogeneous condensation occurs in the range 0,4 µm- 10 µm, (Lind, 2000; Haynes et al, 1982; Davison et al, 1974) and to a great extent when the particle diameter is < 5 µm, due to the high specific surface of the small particles. In addition, due to their high ratio surface/volume, small particles will cool down quicker, and this enhances the condensation rate.

It is possible that a high particle loading offers an enhanced condensation medium. Experimental results (Scotto et al, 1994) indicate that the increased temperature quench- rate increases the emissions of small nuclei undergoing homogeneous nucleation; this suggests that the temperature-cooling rate may influence the nature of the size-segregated aerosol produced.

The temperature/time history of the flue gas in a large-scale and test-scale facility should therefore be similar as much as possible, too. However, test-scale facilities generally have a shorter residence time, and a faster cooling rate with respect to large-scale boilers.

From these observations, it is clear that information on the speciation of the elements (which can be provided by the equilibrium calculations) is needed to evaluate the path of the toxic trace elements.

This short qualitative analysis shows that, under the assumptions of macroscopic-combustion criteria fulfilled, as well as of temperature of gas cooling/gas cleaning devices, it is possible to apply the enrichment **profiles** obtained in a test-scale unit to large-scale plants. Thus enrichment profiles will be useful to furnish qualitative indications, whether the metal will be preferentially captured in the bottom ash, or in the coarse fly ash, or enriched in the fine fly ash, thus representing a potential risk for enhanced emission in the atmosphere.

8. CONCLUSIONS

The present work aimed at analysing the ash behaviour upon co-combustion of paper sludge with coal and coal/biomass blends in fluidised bed combustors. Paper sludge is a waste deriving from the treatment of recovered paper.

The study has been conducted in the framework of a European research project aiming at widening the spectrum of fuels utilised by coal-fired and coal-straw fired fluidised bed boilers, at improving the potential to use energy-containing residues, and at investigating the environmental impact of waste co-firing.

The behaviour of the ash-forming constituents when co-firing is of main interest. Recently, several research activities have shown that, in coal-firing designed boilers, the interactions occurring during the combustion process between the inorganic constituents of biomass and waste fuels with coal ash may cause operational disturbances, due to the occurrence of phenomena like slagging and fouling. This may restrict for technical reasons the utilisation of these unconventional fuels. Therefore, it is of great importance to assess the potential risk in fluidised bed boilers associated to ash deposition on heat exchanger and to bed agglomeration.

Investigations on the behaviour of toxic trace elements, like Cu, Pb, Zn, and Cd, upon paper sludge (co)-firing, are motivated by the occurrence of relevant concentrations of these metals in the sludge, which may be of significant environmental and healthy concern.

For the first time, extensive information on the ash behaviour related to co-firing of paper sludge with coal and with coal/straw blends has been reported. The study has enlarged the current knowledge of the ash-related phenomena when co-firing fuels whose combustion phases are not similarly structured, like coal, straw and paper sludge.

The aim has been to evaluate the potential risk associated to the occurrence of ash-related operational problems and to the fate of toxic trace metals, especially to determine whether they leave the combustor as gaseous emissions, or they are speciated as leachable compounds in the ash. The study has been performed by analysing the experimental results based on detailed mass balances on most of the inorganic species, and by taking advantage of the results of the equilibrium calculations, providing information on the speciation at different temperatures of the various elements of the fuel blends systems upon combustion. Equilibrium calculations were performed at the Process Chemistry Group of Åbo Akademi University, where also a special designed database was used, that took into account the melting of the ash components and the dissolution of the toxic metals into the slag.

The experimental part of the work has been divided into two main sections:

- 1) Combustion test runs of paper sludge as single fuel: An extensive experimental work has been carried out at a fluidised bed test-scale facility (TSF) -30 kWth- to investigate the combustion behaviour of different paper mill wastes. Sludge from primary mechanical separation process and deinking sludge were fired as single fuels.
- 2) Co-combustion test runs: Co-combustion experiments using paper sludge as auxiliary fuel with coal-based blends and coal/straw-based (50%/50%) blends were performed at the TSF. In these blends, paper sludge replaced coal up to a share of 25 %, thus covering realistic fire-blending ratios for a realistic industrial implementation.

These investigations were done in order to acquire detailed knowledge on the combustion behaviour of these fuel blends to be fired in a CFB 80 MWth boiler, belonging to a CHP plant, located in Grenå, Denmark. The main fuel blends of the boiler are coal or coal/straw blends (maximal 50/50 on an energy basis); the investigations were motivated by the interest to enlarge the spectrum of the fuel blends to be fired in the boiler, and to replace the coal share of the blends.

Generally, a good agreement has been found between equilibrium calculations and experimental results with respect to the elements partitioning in the various ash streams coming out at high temperature, medium temperature, and low temperature locations in the facility.

Compared to the other wastes from recovered paper processing, paper sludge is a lighter, less fibrous and more reactive fuel, with lower ash content. The comparison of paper sludge and deinking sludge with respect to the combustion behaviour has shown that differences with respect to formation of bottom ash and sintering phenomena do exist. Upon paper sludge combustion, an ash coating on the bed surface constitutes the bottom ash. Its melting point, according to the equilibrium calculations, is much higher than the usual bed temperature range. Fly ash is formed by a multitude of small agglomerates, deriving probably from mineral matter sintering phenomena. Mineral matter transformation occurs during the combustion process, leading to the formation of a (aluminium)-silicates based fly ash. Generally paper sludge is characterized by a high chlorine content, which will be partly retained in the fly ash as condensed alkali chlorides, the rest forming HCl to a high extent. The toxic trace metals under investigation (Cu, Zn, Pb, Cd, and Mn) were scarcely emitted in the flue gas, the emissions being lower than the limits set by the new EU incineration directive. Leaching analysis supported the result that they are bounded mostly as not leacheable forms in coarse and fine fly ashes, thus proofing the formation of silicates-containing compounds indicated by equilibrium calculations.

Based on the results of the experimental campaign of co-combustion of coal and coal-straw blends with paper sludge in the test-scale combustor, it was concluded that co-combustion of paper sludge with coal could be performed without significant ash-related operational problems in blends covering low shares of paper sludge (here studied up to 25 %). Results of coal/paper sludge blends combustion tests indicate that co-firing enhances formation of alkali sulphates and alkali aluminum silicates in the fly ash, as a result of interaction between alkali and kaolin minerals. This provokes Cl release as HCl in the flue gas from the furnace. The size and consistence of Ca-enriched agglomerates in the bed did not provoke any disturbance in the fluidisation process.

On reverse, upon combustion of paper sludge with a high-alkali, high-chlorine content biomass like straw, interactions between alkali from straw and Al and Ca from paper sludge occur at high temperature. This can lead to bed agglomeration phenomena due to enhanced ash melting. Furthermore, condensation of alkali chlorides on fine fly ash along the flue gas path is enhanced when co-firing. The occurrence of these phenomena may limit the share of paper sludge replacing coal in coal/straw blends. This result is important, because it can be easily extended to other biomass fuels characterised by high alkali-content, and for which paper sludge represents a potential auxiliary fuel.

One of the main topics of the study was the phenomenology of bed agglomeration phenomena when co-firing coal/straw/paper sludge based blends. Special emphasis has been given to the comparison of the experimental studies with the theoretical prediction of bed agglomeration tendencies when co-firing. Melting curves, from equilibrium calculations, describing the composition and the amount of ash melt vs. the fuel blend composition, correlated well with the agglomeration tendencies observed when increasing the amount of paper sludge in the fuel blend.

One very important finding of the bed agglomeration study is related to the influence of the fuel physical properties on the local temperature conditions in the fluidised bed combustor. The results of this work emphasise the importance of a correct determination of the particle temperature in a FB combustor, especially for the prediction of bed agglomeration phenomena and ash melting behaviour under typical operative conditions of a FB boiler.

The accurate description of the local ash-melting phenomena becomes even more important for a fuel like paper sludge, which undergoes easily fragmentation and attrition.

The impact of the ash-forming constituents of paper sludge on Cl enrichment in fine fly ash was evaluated; it was observed that kaolin enhances Cl-release in the flue gas, while limestone enhances Cl capture on the coarse fly ash fraction. These results are of interest in the optimization of the competing mechanisms of Cl capture/formation of HCl during co-combustion. Co-combustion test runs, performed in a similar test-scale FB boiler with wood/bark and wood-based blends, confirmed the results obtained for paper sludge. Attention must be paid to the increase in HCl emissions that occurs with Al-based additives. This may, in dependence of the Cl-fuel content, limit the portion of waste-based fuel that can be used in co-combustion, without exceeding the new limits for HCl in EU legislation. The investigations performed under BFB conditions, are promising also for CFB conditions, characterised by higher fluidisation velocities regimes.

The fly ash agglomerates formed upon co-combustion of paper sludge, composed of small and sintered particles, provide a high surface area for gas-to-particle transformation routes. The occurrence of a high ash heterogeneous surface area enhances the gaseous species condensation on solid particles or the chemical reactions, which is advantageous for the capture of toxic trace metals, (Cu, Pb, Cd, and Mn) that vaporise in the combustion chamber, at high temperature locations. This means that the potential environmental impact associated to the toxic trace metal concentration in the waste constitutes a risk to a less extent, as the metals will be less released in the flue gas. With the exception of Cd, negligible shares of the toxic trace metals were found in the flue gas upon co-combustion test runs. The emissions of toxic trace metals under investigation were always below the limits prevailing in the EU according to the new incineration directive. Furthermore, the toxic trace metals were not found to form water-leachable compounds in the fine fly ash particles, in consistence with the results of the equilibrium calculations displaying the formation of silicate-phases based compounds.

The validation of the TSF investigations was conducted by performing a comparison with an experimental campaign of an industrial-scale boiler. The comparison was focused on the composition of different ash streams. Dissimilarities between the two facilities related to boiler construction, ash recovery system, gas and particle temperature-time history in the combustion chamber and along the flue gas path, restricted the validity of the comparison. The difficulties of performing reliable mass balances in a large-scale unit and of getting a large-scale boiler into equilibrium complicated the scale-up procedure. Similarities were found in the partitioning of elements like Cl, K, S in the fly ash streams and in the enrichment of Cd, Pb, and Zn.

The study opens questions about the transferability of the results obtained in a small-scale facility. Scale-up of fluidised bed boilers has been so far concentrated more on hydro dynamical similarities, rather than on combustion parameters. Furthermore, no rigorous scale-up approach has been undertaken so far with respect to the ash behaviour. With the support of recent experimental findings, this study shows that there is a good potential to predict the ash behaviour by means of investigations at small-scale, under the condition of running under similar operative parameters like fuel, air ratios, flue gas temperature/time history. It is therefore very likely that the phenomena described in this study will occur also in large-scale facilities operating with similar combustion parameters.

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Appendix I

Legislative background

When this study was initiated, in January 1998, the emission limits of energy production set by the EU legislation, including SO₂, NO_x and particulates, were applied to all the studied fuels (88/609/EEC). Tighter emission limits existed for waste incineration and hazardous waste incineration (89/369/EEC¹ for new incineration plants and 89/429/EEC² for old incineration plants), but they did not concern the case of biomass residues and wastes, like paper sludge, under co-firing with the traditional main fuels.

Preparation of a new directive for co-combustion was started in the middle of 1998 (version 98/0289SYN). Political agreement of the content of the new directive for co-incineration (and co-combustion) in the EU was achieved on June 1999. The Commission prepared the draft directive COM 99 (330) on the basis of this agreement. The key objectives of the new Directive were the extension of the scope of Community legislation to cover the incineration of non-hazardous, non-municipal waste, as well as the hazardous waste, previously excluded from the Council Directive 94/67/EC on hazardous waste incineration, to introduce the emission limits for plants that co-incinerate waste; furthermore, to set a new requirement that the heat generated in the incineration process shall be recovered as much as possible.

The European Parliament accepted the final version in November 2000 and the directive officially prevail since the middle of January 2001. The final version is closer to the Commission's version- COM (99) 330- published in autumn 1999, than to the tighter version made after the second reading of the Parliament.

According to the new legislation, pulp sludge and paper sludge are classified as it follows: they will be classified to biomass if they are "co-incinerated at the place of production and the heat is recovered". This means if they are combusted at the place of production, a pulp and paper factory, which usually utilise bark or coal-fed fluidised bed boilers.

In Germany, the 17. BimSchV³ regulates the combined combustion of waste-derived fuels and fossil fuels. When the fraction of waste in the fuel blend is lower than 25% (based on thermal

¹ Commission of the European Communities : Council Directive 89/369/EEC on the prevention of air pollution from new municipal waste incineration plants

² Commission of the European Communities : Council Directive 89/429/EEC on the prevention of air pollution from old municipal waste incineration plants

³ Verordnung über Verbrennungsanlagen für Abfälle und ähnliche brennbare Stoffe (17 BimSchV- Verordnung zum Bundes-Immissionschutzgesetz)- 23.11.1990 (BGB1.I.S. 2832)

input), the “mixing rule” is applied to determine the emission limits. This means that the limits to the emissions are obtained by averaging the limits applied for waste incinerators and for fossil fuel in power plants (those are listed in the 13. BimSchV⁴) and weighed with the thermal input of the waste with respect to that of the coal. If the share of the waste in the fuel blend exceeds 25%, then the emissions limits for waste incinerators are applied.

According to the previous EU legislation (89/369/EEC), the sets for emissions for co-combustion were much more permissive than the German ones. In the new one, the sets for waste incineration are the same of the 17. BimSchV. For co-incineration of waste fuels, the emission limit for each pollutant is calculated as the average limit for waste incineration and the limit value for the combustion; if the waste fraction exceed 40% on an energy basis, then the limits prevailing are those for waste incinerators. The mixing rule applies also in the new legislation, and the weighing medium is considered the volume of the flue gas, similarly to the weighing the contribution to the overall heat released. The emission limits of the previous and current legislation are shown in **Table I**.

According to the new co-incineration and co-combustion directive (accepted in the third reading of the European Parliament in November 15, 2000), emission limits for energy production prevail with fuels like: wood (containing spruce heartwood and bark), straw and coal. Limits exist also for NO, SO₂ and particulates.

The new emission limits for co-incineration will be tighter than those prevailing or suggested earlier to waste incineration because the reference O₂-content has decreased from 11 vol% O₂ to 6 vol% O₂. This means alone a decrease of a given limit value by 33%. Residence time of 2 s at > 850 C (after the tertiary air inlet) is required.

Regulated toxic elements are partly different in the new directive compared to the old legislation for waste incineration. Mn, Sb, V and Tl have replaced Zn and Se.

This document allows higher NO_x and SO₂ emissions for fluidised bed co-combustion plants than for waste incineration plants until 2008. One reason is probably the much higher efficiency of fluidised bed CHP co-combustion plants compared to co-incineration plants. Limits for SO₂ and particulate are stricter than the previous legislation, indirectly favouring only low-sulfur content fuels to be co-incinerated.

Another important limit is concerning HCl and the emission limit set for co-incineration of waste is equal to 10 mg/Nm³ @ 6 % O₂.

⁴ Verordnung über Großfeuerungsanlagen (13 BimSchV-Verordnung zum BundesImmissionschutzgesetz)

	17. BimSchV	COM(98)0558 Annex II and V ⁵	89/369/EEC
Cd+Tl	50 ^{5,6}	50	
Hg	30 ⁷ 50 ⁸ 50	50	
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V+Sn	500	500	
Cr+Cu+Mn+Pb			5000 ⁶
Ni+As			1000 ⁵
Cd+Hg			200 ⁵
HCl		10	
Dust			

Table I: German regulations, previous and current EU regulations on waste incineration emission limits. All values are in $\mu\text{g}/\text{Nm}^3$ on dry basis with the exception of HCl and dust (mg/Nm^3)

22.06.1983 (BGB1.I.S.719)

⁵ Sampling time is minimum 30 min and max 8 h. Limit refers to a concentration of 6% O₂ in the flue gas

⁶ Sampling time is minimum 30 min and maximum 2 h.

⁷ Daily average;

⁸ Half-hour average.

⁶ Limits refer to a concentration of O₂ in the flue gas of 11%

Appendix II

Physical and chemical characterisation of fuel/ash samples

Elementar analysis has been performed by simultaneous determination of C, H, N, S. The analysis has been always conducted with the device VARIO, (a product of the company Elementar) according to the standards of ASTM D 5373. C, H, N and S are determined by means of an oxidative combustion, leading to the formation of the products CO₂, H₂O, NO₂, SO₂, SO₃ (and N₂), from whose measurement the concentration of C, H, N, S can be determined.

Chlorine and Sulphur

With respect to chlorine, the fuel must be incinerated in a muffle oven (DIN 51727, standard for coal) or combusted in a bomb digester, where Cl in gas form is later dissolved in a NaOH 0,25 molar solution (DIN 51577). After that, the two possible analysis methods are titration or IC (ion-chromatography) of the eluate. The bomb digestion has been mostly used for reasons of the high precision, (Siegle, 1999) and usually followed by the titration. For ash samples and eluate samples, usually the titration method has been used; often a comparison with the IC method has been performed.

Sulphur determination is based on the assumption that the residual ash after combustion of the fuel sample in the muffle oven does not capture the volatile species: this may be not the case for Ca-rich ash, for which the capture may be instead high. Similar effects may arise for Cl, for which it is known that particularly Ca may contribute to the binding of Cl and to the formation of CaCl₂. There is not yet a standardised procedure that takes into account the Sulfur and Chlorine content in the residual ash⁷.

In this study, the non-combustible ash remaining after the combustion at 815 °C in the muffle oven has been analysed, too, and the Sulphur and Chlorine content has been determined respectively by means of elementar analysis and titration.

Proximate analysis

Moisture, ash, volatile and fixed carbon, have been all determined by means of the same instrument (LECO).

⁷ In this study, S and Cl content analysed in the residual ash were close to the instrument detection limit, and therefore no relevant deviation from the standards has been observed.

Moisture content has been determined by means of thermogravimetric analysis, where the sample heated up to 106 °C under a N₂ atmosphere, keeping temperature until the weight loss is smaller than 0,2 % (according to DIN 51718). Volatile content has been also determined by means of thermogravimetric analysis, with the sample heated under a N₂ atmosphere, keeping it to a temperature up to 900 °C for 7 minutes (according to DIN 51720). The ash content is determined by keeping the sample to a temperature of 815 °C under an oxidising atmosphere until the weight loss is smaller than 0,2 % (according to DIN 51719).

Heating value

The high calorific value of the fuels has been determined by means of a bomb calorimeter (according to the DIN 51900 T3)

Ash composition.

Standard fuel ash characterisation starts with the ashification of a sample which is left at a temperature of 815 °C for 1 hour (DIN 51719); this procedure is indicated for coal, but not for biomass or other wastes, for which a lower temperature, 550 °C, is preferable (Siegle, 1999). For biomass and waste fuels, the carbonate content may be high, and it can be already destroyed at temperatures as low as 600 °C. To verify the carbonate content of the ash, the analysis of C content by means of elemental analysis has been additionally performed.

For this study, the XRF technique equipped with a wavelength-dispersed detector (WD-XRF) was mostly used. The measurements take place after ash fusion with lithium-tetraborate.

Detection of water-soluble species has been performed by means of AAS analysis on eluate). Cl⁻ and SO₄⁻ and, generally, concentrations of water-soluble species, were analysed by ion chromatography.

Toxic trace metals

Trace metal (like Cu, Zn, Mn, Pb, Cr, Ni) content in the ash and fuel has been determined by means of flame-atomic-absorption-spectroscopy (AAS) methodology, after diluting in aqueous solution the sample obtained by wet ashing (dissolution) in a mixture of HNO₃/ HF, and followed by microwave digestion. (DIN 48 406). AAS analysis is more sensitive to the trace elements than the XRF.

Usually the shares of HNO₃/HF and the total content of the aqueous solution have been chosen differently for each ash sample. The eluate samples from the wet-chemical methods, taken

during the combustion test runs, had not been digested/acidified further, but directly brought to AAS.

Particle size distribution

The particle size distribution of the ash samples has been determined by means of laser diffraction based measurements, (equipment: Malvern), to interpret the measurements results, and the method of Fraunhofer has been later applied.

Microscopy and X-ray diffraction analysis

Analysis of crystalline phases for some selected fly ash samples was performed by means of X-ray diffraction. A CuK- α emission source was utilized, with an analysis angle of 6°-79°, step angle 0.016° and step time 0.3 sec. For characterisation of supermicron and submicron ash particles, larger magnification were required, and thus high resolution SEM was used. Energy dispersive spectroscopy (EDX) was used to obtain qualitative information of particle elemental composition.

Gas Measurements

The Schema of the flue gas measurement arrangement and analysing equipment is shown in **Figure 1**.

The following equipment was used:

1. O₂/CO/CO₂: Rosemount Binos 100 (ND-Infra Red)
2. SO₂: Rosemount Binos 1104 (UV)
3. NO/NO_x: Eco-Physics (Chemiluminescence)
4. N₂O: Horiba (UV)

Determination of toxic trace metals emissions

The determination of the toxic trace metal concentrations in the flue gas has been effected by means of discontinuous wet-chemical analysis methodologies, following a slightly modified EPA29 method⁸. A flue gas sample is withdrawn non-isokinetically; particulate matter is then collected in a heated filter probe, and gaseous emissions are then dissolved into an aqueous solution (a first series of impingers containing an acid solution-5% HNO₃⁹- a second series of

⁸ <http://www.epa.gov/ttn/emc/promgate/m-29.pdf>, updated 2000

⁹ The method EPA 29 requires the utilisation of a solution of HNO₃/H₂O₂. However, it was observed that the water peroxide disturbs the AAS measurements and therefore it has been eliminated, other sources (Aho, 1998)

impingers containing a 4% KMnO_4 /10% H_2SO_4 solution). It is assumed that the acid solution captures Hg under oxidised form, while the second series captures Hg under elemental form. All the others trace metals are assumed to be captured in the first series.

This approach is common to other standardized methods for measuring trace elements (Miller et al, 1999), based on the “wet chemical” methodology, in combination with particulate phase element trapping in filters, which are kept at the same temperature of the flue gas. The filter is made of heavy- metal free quartz wool, which, according to EPA indication, is the best material to avoid any contamination with any external metal; quartz wool filters have also a negligible reactivity to SO_2 absorption. Teflon® is the material used for the probe fitting in order to avoid metal contamination. Quartz glass was used for the probe nozzle and the probe line; for other measurements the quartz glass has been replaced with Teflon® lines; without causing any relevant difference in the results. The filter has been heated electrically in a temperature range 120 ± 20 °C. The impingers, containing the solutions, are connected with leak-free, non-contaminating fittings. The first impinger is used for the moisture trap; two impingers are then filled up with the HNO_3 solution and the other two with the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution. The impingers (kept in a cold ice water bath) are followed by a silica gel tower, a main valve with gas-flow regulator valve, a pump, and a gas counter (**Figure 2**). The gas flow rate (dry) was usually in the range 7-10 l/sec, and a corresponding total pumped flow of 1-1.5 Nm^3 was necessary for a the absorption of the necessary quantities for the chemical analysis. Usually the sampling line has been also washed out with a HNO_3 -acidified solution, and later analysed with AAS, to avoid any losses in the recovery of the elements.

The mass of the particulate matter lying on the ultra-fine filter has been weighed, dried and its composition analysed (sulphur and chlorine) with IC methods.

HCl emissions

Determination of HCl content in the flue gas has been performed by means of wet-chemical, discontinuos methods, where the non-isokinetical withdrawing of the gaseous samples, and the particulate removal has been effected according to the same methodology described for the toxic trace metal absorption; in this case, however, the impingers were filled up with distillate water. Ionic-Cl content is later determined by means of titration or IC. The method is based on the assumption that there is a direct, linear correlation between Cl in ionic form absorbed in the

have found out that the utilisation of HNO_3 only furnishes a sufficient degree of acidification required for the metal capture.

bottles and HCl content in the flue gas. Interference with other Cl ionic form, like alkali chlorides is therefore excluded.

Leaching analysis

The fuels were also investigated by means of a chemical fractionating procedure in order to characterize the different solubility of the ash elements. The utilised methodology is described in literature (Benson, 1995). There are several different leaching procedures reported in literature (Baxter, 1994) aiming at characterizing the different mobility of alkali and other inorganic constituents according to the chemical bound in the fuel structure. These leaching procedures are extremely useful to characterize both fuels and ash, and can provide important information on the environmental impact if the fuel and ash are recirculated back to the soil for deponating. Usually these procedures distinguish between different types of inorganic material according to their solubility in a series of increasingly aggressive solvents. Typical ash-forming constituents that are leached with water are alkali, if associated with S and Cl, and light carbonates. The acid leaches typically out carbonates and sulfates of calcium and magnesium. The fraction that is not soluble (as heavy carbonates, silicates, clay minerals, oxides and sulfides) is assumed to be unlikely to volatilize or to interact with other particle. These procedures have been widespread applied to coal characterization, and have recently been extended to biomass.

In this study, leaching analysis has been used to characterise the difference of "reactivity" of the ash constituents upon combustion, due to their mode of occurrence in the fuel. The procedure followed to characterise both fuels and ash is based on a two-stage leaching method, and the solutions used are, respectively, distillate water and HCl (10%).

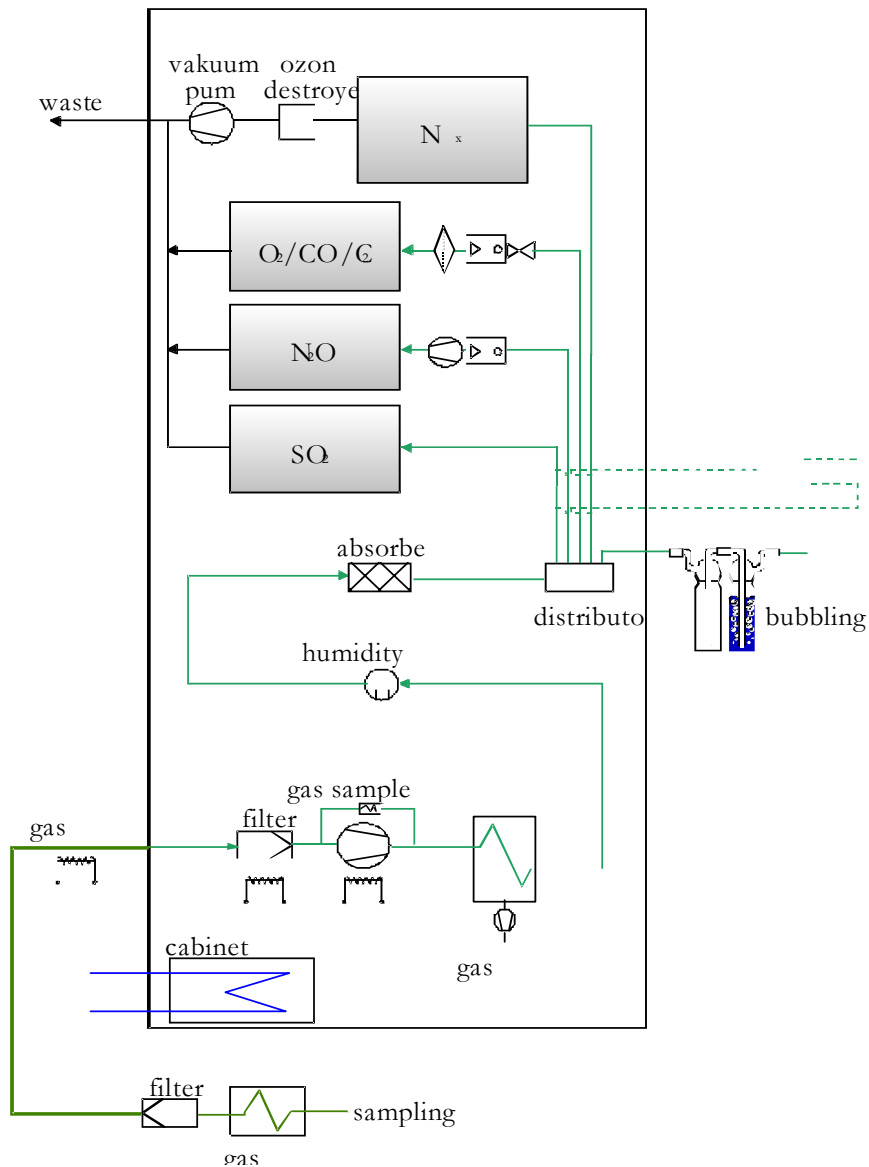


Figure 1: Schema of the flue gas measurement arrangement and analysing equipment

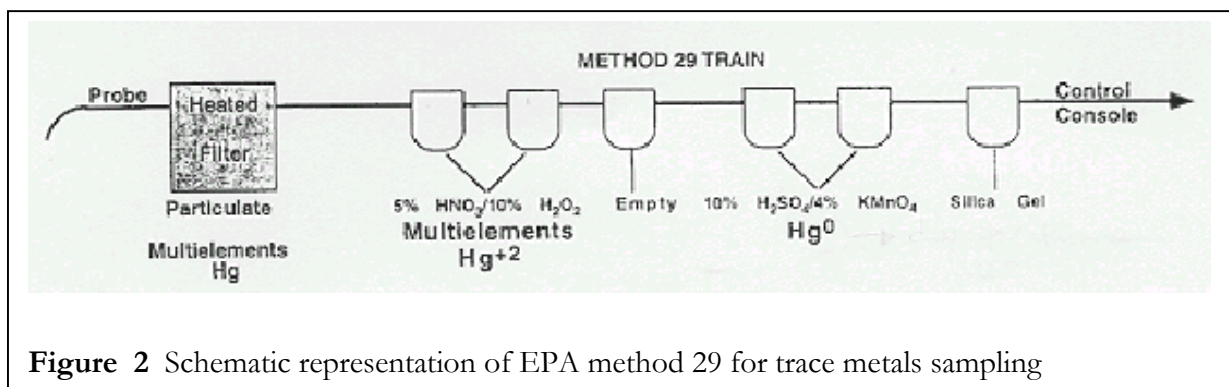


Figure 2 Schematic representation of EPA method 29 for trace metals sampling

Appendix III

Standard deviation error for mass balances

When performing the mass balances, typical sources of error are:

- 1) Loss of elements within the plant
- 2) Loss of elements within the sampling equipment (absorption in sampling probes)
- 3) Assumptions of the plant operation: concentrations fluctuations in the raw material, fuel, sorbents, etc.

4) Methods of ash sampling and flue gas sampling

It is well known that the sampling and analysis methods which are currently available for determination of toxic trace metals, and generally, wet-chemical, discontinuous measurements methods, are problematic and prone to error. The majority of the published data are related to mercury. Millers and others (1999a) noted margin of errors for most the trace elements of about $\pm 20\%$. Tolvanen et. al. (1995) reported a percentage variability for triplicate testing measured at the baghouse entrance quite high for Se, Hg, Mn, ($\pm 50\%$), and less high for Cu, Zn, ($\pm 20\%$); Cd ($\pm 30\%$).

The small scale of the TSF allows the plant to reach the steady state in a relatively short time, therefore problems associated to the operation of the plant are considered to be minimal.

For this study, the standard deviation error for the total recovery rate is reported in **Table 1**. For the calculations, basic parameters are:

- 1) the standard deviation error of the analysis methods;
- 2) the estimation error of the mass flow of each input and output stream.

In these calculations, for all the elements a conservative error ($\pm 10\%$) has been estimated for the bottom ash output streams. The ash originating from cyclone and filter is assumed to have an higher degree of homogeneity in comparison to the bed ash and the fuel blends samples; composition fluctuations in the samples due to the simultaneous presence of different fuels is also believed to have a minimal degree of inhomogeneity. Estimated precision of the sampling is based on the same repeated measurements: for tritration, and for AAS, elemental, and XRF analysis, the estimated precision was up to $\pm 5\%$. After repeated measurements, the negligible contribution of sand material to addition of trace elements has been omitted.

Table 1 reports the calculations for the case of paper sludge only, but similar calculations have been performed for the other fuel blends.

The results show that, with the exception of K, the error estimation of the total recovery rate for the main ash forming constituents is less than 15 %; for some trace elements, this can be higher, as the error gets larger when the concentrations in the raw fuels gets closer to the detection limit of the instrument (Pb, Cd, Hg,) even higher, due to the very low concentration in the fuels. For Cl, the high inaccuracy derives from the large fluctuations in the fuel samples of paper sludge

Element	Error (%)
Cu	± 15
Zn	± 11
Mn	± 11
Pb	± 20
Cd	± 20
Cl	± 17
Hg	± 29
S	± 13
K	± 22
Ca	± 12

Table 1: error estimates (%) for the total recovery rate (bed ash + fly ash-coarse and fine fractions + -if sampled - flue gas) of ash-forming constituents.