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Experimental studies on pulp and paper mill sludge ash behavior in fluidized bed combustors

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Abstract

Ash formation during the fluidized bed combustion (FBC) of pulp and paper mill sludges has been experimentally studied on an industrial and bench scale. The methods included aerosol measurements, chemical and crystalline composition analyses, thermogravimetry and electron microscopy. Fly ash mass and number size distributions and elemental enrichment in submicron particles and bottom ash were measured. Fly ash, bottom ash and ash deposits were characterized and their formation mechanisms are discussed.

Fly ash included over 90 % of the ash-forming species, the rest remaining in the bed. The ash-forming minerals were fine paper-making additives, clay minerals and calcite, located within the sludge fibers. During combustion the minerals sintered, forming porous agglomerates. The mineral structure was transformed into amorphous phases, calcium silicates and alkali silicates in the fly ash. Increased ash residence time in the furnace enhanced the silicate formation. The fly ash mass mean size was 7.5-15 μm and the ash did not fragment much into submicron particles. The supermicron particles included 93.6-97.3 % of the fly ash.

Condensation of the volatilized inorganic species formed spherical submicron particles in the fly ash. Their mass concentration was almost negligible when co-firing paper mill sludges and wood. Correspondingly, no significant enrichment of the volatile inorganic species or trace elements in the ultrafine ash was detected during paper mill sludge and wood firing suggesting that the fraction of the volatilized inorganic species in the paper mill sludges was low. Results from pulp mill sludge and bark co-firing were different. This fuel mixture produced a clear mass mode below 0.3 μm , presenting 2.2-5.0 weight-%

of the fly ash. The condensed species included K, Na, S and Cl. Their mass fraction was higher in the pulp mill sludge than in the paper mill sludge and evidently this resulted in increased volatilization and formation of condensed particles. The following trace elements were enriched in the submicron ash during pulp mill sludge and wood co-firing: As, Cd, Rb and Pb. The main part of the volatile species was not captured in the condensed ultrafine particles, but in the bulk ash. Presumably, this was due to the high surface area concentration in the bulk ash, which enhanced the gaseous species condensation on the bulk ash and chemical reactions with solid particles. Sludge moisture reduced the inorganic species volatilization. Probably this was due to steam vaporization from the wet particles through the burning layer resulting in decreased combustion temperatures on char surface and a lower fraction of formed char.

During sludge combustion the largest ash particles, over 200-300 μm , were accumulated in the bed due to their size. Their mass fraction in the bed was in the order of a few percent in the industrial units and they did not cause bed agglomeration. Lower fluidization velocities were used on a bench scale, where the large particle fraction grew in an unlimited manner. Sintering of these particles resulted in gradual bed defluidization. Ash was also accumulated in the bed as micron-size particles adhered to the sand surface forming a sintered layer. Bench-scale tests showed that this type of layer, formed during bark combustion, initiated bed agglomeration and resulted in defluidization without combustion at 988 °C. With pulp and paper mill sludges the layer formation was not connected to bed agglomeration at the studied temperatures up to 1,000 °C. Presumably, the bark-derived K species in the layer decreased the ash viscosity and triggered bed agglomeration. Trace elements were not accumulated excessively in the bed.

Ash deposits were formed on the furnace wall above the bed. Ash and sand particles were deposited on the surface roughness probably from the down-flowing particle flux near the wall. Ash sintering densified the structure. Condensed or molten ash species were not detected in the structure. The ash viscosity was lower in the pulp mill sludge resulting in larger deposits than during paper mill sludge firing. Calculations indicate that when the ash viscosity is less than 1,000-3,000 Pa s, large ash and sand particles are incorporated in the deposit.

Preface

The studies described in this thesis were carried out at the Aerosol Technology Group of VTT Chemical Technology and at the University of Toronto, Chemical Engineering Department. I wish to express my gratitude to the researchers in both groups. I am greatly indebted to Dr. Esko I. Kauppinen for supervising my work and for his comments on this manuscript. My thanks are also due to Prof. Honghi Tran and Prof. David Barham for the fruitful collaboration and guidance that initiated my studies. I dedicate my warmest thanks to the Laboratory of Applied Thermodynamics of Helsinki University of Technology, especially to Prof. Markku Lampinen.

This research was funded by the Technology Development Center's LIEKKI research program, the Foundation of Technology in Finland (TES) and IVO Power Engineering, which is here acknowledged. The writing of this thesis was made possible by VTT Chemical Technology and IVO Research Foundation.

My inspiration for this study originates from the years when I worked as a boiler commissioning engineer at Outokumpu EcoEnergy. The contribution of the people that I worked with, engineers, operators and mechanical workers, is not shown in this text. However, the things that I learned from them were highly valuable during this research.

Finally, I wish to thank my wife Riikka for her understanding and patience during the evenings and weekends that I have spent doing this research.

Doing research is 5 % inspiration, and 95 % perspiration.

Thomas Alva Edison

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Acronyms

AAS	Atomic absorption spectroscopy
AES	Atomic emission spectroscopy
BFB	Bubbling fluidized bed
BLPI	Berner-type low pressure impactor
BET	Brunauer, Emmet and Teller measurement of specific surface area
CFB	Circulating fluidized bed
C_{fix}	Fixed carbon content
DMA	Differential electrical mobility analyzer
DTA/TGA	Differential thermoanalyzer/Thermogravimetric analyzer
EDS	Electron dispersive spectroscopy
ELPI	Electrical low pressure impactor
EPMA	Electron probe microanalyzer
ESP	Electrostatic precipitator
FE	Field emission
FBC	Fluidized bed combustor
HR	High resolution
IC	Ion chromatograph
ICP	Inductively coupled plasma spectroscopy
IEA	International Energy Agency
MS	Mass spectroscopy
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
SEM	Scanning electron microscopy
SMPS	Scanning mobility particle sizer system
tds	Tons of dry solids
TEM	Transmission electron microscopy
TEOM	Tapered element oscillating microbalance
TMP	Thermomechanical pulping
U_{mf}	Minimum fluidization velocity
U_0	Superficial fluidization velocity
WDS	Wavelength dispersive spectroscopy
XRF	X-ray fluorescence
XRD	X-ray diffraction

Publications

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6. Latva-Somppi, J., Moisio, M., Kauppinen E. I., Valmari, T., Ahonen, P., Tapper, U. and Keskinen, J. Ash formation during fluidized bed incineration of paper mill waste sludge. Accepted in the *Journal of Aerosol Science*.
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Author's contribution

This research has been carried out at the Aerosol Technology Group of VTT Chemical Technology, Finland (Publications 4-7) and at the Chemical Engineering Department of the University of Toronto, Canada (Publications 1-3), where I worked as a visiting scientist in 1992-93. The publications are numbered in chronological order and they concentrate on the following issues. Publication 1 presents the characterization of the thermal behavior and ash-forming species of paper mill sludge. It is based on my experimental work at the University of Toronto and the paper was written under the guidance of Prof. Honghi Tran and Prof. David Barham. Publication 2 reports results from pilot-BFB studies during the combustion of paper mill sludge. My contribution was to characterize the ash and measure the fly ash particle size distributions. The main author of Publication 3 is Prof. Tran and it presents results from a paper mill firing sludge in a suspension combustor. I was responsible for carrying out the field tests and characterizing the sludge and ash samples.

Publications 4-7 are based on my experimental work at VTT. These papers concentrate on defining the inorganic species volatility during combustion and the effect that this has on the ash-related problems. Several co-authors have assisted in the measurements and Dr. Esko Kauppinen has supervised the work. Paper mill sludge combustion in industrial fluidized bed combustors is thoroughly described in Publications 4-6. The characterization of the main ash species is discussed in Publication 4 and the fate of trace elements in Publication 5. Publication 6 includes a profound discussion on ash volatility and ultrafine particle formation when combusting paper mill sludge in industrial units. Publication 7 compares results from an industrial BFB and a bench-scale unit co-firing pulp mill sludge and bark.

1. Introduction

1.1 Definitions

Several disciplines are involved in combustion research. Therefore, some definitions require special attention. The first is **ash**, which is a combustion product formed from fuel-inherent inorganic species (Benson et al., 1993). Fuel includes **ash-forming species**, not ash. However, it is typical to report ‘fuel ash content’, which is the residual weight fraction of a fuel sample after heating at a certain temperature. The ash-forming species are often transformed during the ashing, hence special attention should be paid to the interpretation of the results.

The ash particles are typically divided according to their size. The smallest particles are called **finest**, which are below 2 μm (Hinds, 1982). The larger particles, which typically form the bulk of the ash weight, are called **bulk ash**. Another division can be made between the **submicron ash** and **supermicron ash**. Also the word **ultrafine particle** is used. This refers to the smallest particles, which are typically formed via condensation of volatilized species. In this study the limiting size is 0.3 μm .

The definition of **absorption** is broad. In this presentation it includes all the mechanisms that incorporate gases, liquids or solids into particles. **Adsorption** is defined as the attachment of particles to a surface (Atkins, 1994). This can occur via physical forces, called physisorption, or by chemical binding, which is chemisorption. In this presentation the following physical forces are referred to: van der/Waals forces, cohesive forces and electrostatic forces.

The boundary layer can be defined according to many criteria. In this work it is used to describe the area around a burning particle, where the highest temperatures are located and combustion reactions mainly take place.

In a **chemical reaction** a new chemical compound is formed. The reactive species can be in different phases and especially in the ash studies the chemical reactions between gaseous and solid species are important.

The meanings of **coalescence** and **fusion** overlap and not easily defined. In this presentation coalescence is the phenomenon where particles come together and form an entity in which the original particle shape is lost. The driving force in coalescence is typically melting or sintering. Fusion refers to the particle's visual appearance, rounded and smoothed surfaces. Analyses of ash softening and fluid temperatures are based on the shape of an ash sample when heated, hence these results are often called fusion temperatures. Fusion is a result of various phenomena, hence interpretation of the results can be difficult. Even though several authors have addressed this problem (e.g. Wall et al., 1995, Öhman, 1997), the standard method has not yet been replaced by a more accurate one. Ash **stickiness** or **softening** is often named as the reason for particle agglomeration or deposition. Again, definitive descriptions are scarce. Here, stickiness is understood to be a particle surface property indicating how readily it is attached to surfaces. It explicitly refers to supermicron particles because for them the surface forces are sufficient for adhesion. Softening is related to stickiness. The particle surface can be softened by melting or decreased viscosity and therefore becomes sticky.

Condensation is the process that transforms gaseous species into a liquid or solid phase. This can happen by the formation of new particles, which is called nucleation (Seinfeld, 1986). Nucleation is also known as homogeneous condensation (Jokiniemi and Kauppinen, 1995). In heterogeneous condensation the volatile species form a layer on an existing particle surface. This requires lower vapor pressures than nucleation and is often the main type of condensation in combustors.

Phase transitions and **sintering** are important ash-forming mechanisms. The temperatures of vaporization, melting and condensation can be calculated according to thermodynamic data and the results can be checked by measurements. However, ash structures are multi-component systems, and instead of clear phase transitions sintering is probably the most common feature in ashes. According to German (1996), sintering is a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events often occurring on the atomic scale. Sintering is based on material diffusion in the solid, liquid or vapor phase. In the fluidized bed research bed sintering is also referred to as agglomerate growth in the bed or defluidization. This can be misleading, because phenomena other than sintering,

e.g. ash melting or condensation, might also cause the agglomerate growth. Here the **bed agglomeration** refers to bed coarsening via sand or ash particle agglomeration. **Defluidization** takes place when cohesive forces between bed particles exceed the forces exerted by fluidization gas. In bed operation this is typically seen as a rapid decrease of bed pressure and a cessation of the bed movement.

Particle size refers to diameter in this thesis. The concept of diameter includes an assumption of sphericity, which is rarely valid for ash particles. To understand what particle size means, one should know how it is measured. The ash particle size measured by microscopy refers to the visual size. Several methods have been developed to calculate an equivalent diameter of an irregular particle (Hinds, 1982). Mass size distributions in bulk ashes are typically measured by mechanical sieving. Here the size refers to the sieve mesh size, which is the distance between sieve wires. The particle shape, fragmentation and adhesive forces affect these results, and the practical lower limit is 400 mesh, 44 μm . Wind sieves and impactors classify particles according to the **aerodynamic diameter**, which is the diameter of the unit density sphere (1 g/cm^3) that has the same settling velocity as the particle (Hinds, 1982). If the particle density and shape factor is known, the aerodynamic diameter can be transformed into **Stokes diameter**, which is the diameter of the sphere that has the same density and settling velocity as the particle. Impactor measurements shown in this study are converted into Stokes diameter, because it is a better indication of the real particle size, as measured in microscopy, than the aerodynamic diameter.

The vocabulary of combustor technology cannot be covered here, but some words require explanation for a new reader. **Combustor** and **incinerator** are understood here as synonyms. Burning takes place in the **furnace**. The upper part of the furnace is called the **freeboard**. When the furnace is an insulated vessel without heat exchangers it is called a **reactor**. In a **boiler** heat exchangers are included in the combustor structure. **Primary air** is used for fluidization, while **secondary air**, or over-fire air, is blown into the furnace above the bed and is used for final combustion.

1.2 Background

Pulp and paper mill sludges consist of water treatment rejects separated from the mill effluent. They originate mainly from three sources. Primary sludge comes from the primary clarifier, where the coarse particles are removed from waste water. The concentration of fibers is high and the sludge can be easily dewatered. The sludge resembles wet paper. Secondary sludge originates from the secondary water treatment, which typically is a biological process. This type of sludge is often called biosludge. Less fibers are present and dewatering is difficult resulting in low solid concentrations and paste-like appearance. Similarity with sewage sludge is obvious. The third source is the deinking process, where the recycled paper fibers are separated from paper additives and inks. Deinking sludge includes fibers and high concentrations of inorganic minerals and can be dewatered easily. Sludges are also derived from other processes including e.g. chemical sludge from the chemical water treatment and residual sludge from the debarking process. Sludges are typically mixed before dewatering and the origin of the sludge constituents are hard to trace, which is a problem when studying the effects of separate sludge types on the combustors. Mills are rarely similar in their process configuration, hence the sludge quality varies between mills. However, a clear difference exists between the sludges in pulp mills and in paper mills. The pulp mill sludge includes a higher fraction of secondary biosludge. Another difference is that modern paper mills are typically integrated with a deinking process, which has a significant impact on the sludge quantity and quality. Therefore a division in pulp mill sludges and paper mill sludges is justified and is used in this study.

Sludge production in pulp and paper mills has increased for two reasons. The first is the improvement in water treatment during the last decades. This will also be the trend in the future, and accordingly mills are struggling to close their water circuits entirely. Another reason is paper recycling, which has rapidly expanded during recent years. A paper mill integrated with a deinking process produces typically 100 tds/d of sludge, originating mostly from the deinking plant. This can be compared to the sludge production rate in a large pulp mill being 20 tds/d (Tolvanen, 1997). Finland is a good example of the high sludge production rates in the forest industry. The production was 335,000 tds/a in 1992 and estimates for the year 2000 are 371,000 - 421,000 tds/a. This is more than the sewage sludge production in the whole country, 150,000 tds/a in 1992

(Malinen et al., 1993). Half of the pulp and paper mill sludge was incinerated in 1992. The remaining half was landfilled, however increasing landfilling costs are expected to shift the balance towards incineration. Sludge has also been used as a soil conditioner, but high transport costs and the probable diffusion of toxic compounds into the soil and plants are limiting its use (Anthony, 1995).

Sludge combustion has been successful for several reasons. The first is the ability to generate steam and heat, which despite the low heat value in sludge is still an economical benefit. The second is the reduction in sludge volume and weight resulting in lower landfilling and transportation costs of the combustion ashes. The third reason is reduced pollution. Toxic organic compounds are a potential hazard for landfilling. When incineration is carried out at high temperatures with sufficient residence times and in an abundance of oxygen, the toxic organic compounds can be decomposed. EC legislation for waste combustion requires that the flue gas temperature should be maintained at over 850 °C with a 6 % oxygen concentration for at least 2 seconds (The Council of European Communities, 1993). Measurements in bubbling fluidized bed boilers (BFB) firing deinking sludge showed that the emissions of organochlorine compounds including dioxin, chlorophenol, chlorobenzen, PCB and PAH were, indeed, below the regulatory limits (Dixit et al., 1993, Vayda et al., 1993). Incineration of pulp and paper mill biosludge and bark in a circulating fluidized bed (CFB) did not produce organic chlorinated compounds above the regulatory limits (Halonen et al., 1993). It was further reported that no catalytical de-novo synthesis producing toxic compounds in flue gases was observed, which is a great benefit when compared to the combustion of high-Cl wastes. Several combustion technologies have been applied for the pulp and paper mill sludges, however, fluidized bed combustion (FBC) has been the most successful. One reason is the ability to fire wet fuels with a high combustion efficiency at a low temperature due to the efficient mixing of bed heat. Another reason is the efficient destruction of the toxic organic compounds. The third reason is the low combustion temperatures in FBC, which result in negligible formation of thermal-NO_x, and reduced volatilization of toxic trace metals. A further benefit is that sludges can be flexibly co-fired in FBC with the mills own wood wastes.

Sludge is a new and unusual fuel and boiler operation can be harmed by ash-related problems. The concentration of ash-forming species in sludge is high, and this can easily cause overloading of the ash removal equipment and increased particle emissions. Ash might initiate bed agglomeration and result in unstable combustion or defluidization. If ash is deposited on the furnace walls or heat exchangers, it will decrease the heat exchange capacity in the boiler. These problems have been studied when burning coal or biomass (e.g. Miles et al., 1996, Bobman et al., 1985, Hurley and Benson, 1995), but for sludge only limited information is available. Volatilization of ash-forming species has a significant impact on the feasibility of sludge combustion. The first reason is the fly ash removal from flue gases. The volatilized species are prone to condense and form submicron particles. Unlike the supermicron particles, submicron material is difficult to remove from flue gases (Porle et al., 1995). The second reason is health effects. Submicron particles penetrate into the pulmonary system and have been related to increased mortality (Heyder et al., 1986, Pope et al., 1995). The toxicity of submicron particles is further increased if volatilized trace metals condense on the surface of the submicron particles. The third reason is related to technical problems. Condensation of volatilized species, namely alkali salts, has been found to cause ash deposition during coal combustion (Oakey et al., 1990). Volatilized ash species may also react with steel and can be involved in boiler tube corrosion (Harb and Smith, 1990).

1.3 Objectives

This thesis was motivated by the need to obtain a more profound understanding of ash behavior during sludge combustion. Although sludges already form a significant fuel fraction in the forest industry, they are often co-fired without a knowledge of the possible consequences in ash handling. Current studies concentrate mainly on describing the macroscopic sludge combustion characteristics, e.g. the ability to co-fire sludge with other fuels, and the flue gas emission levels. No presentation of the ash-forming mechanisms with these sludge types is available. The volatilization of the sludge-derived inorganic species has not been measured neither on an industrial or bench scale. Correspondingly relatively little is known of the trace element enrichment in submicron particles or in the bottom ash.

The primary goal in this thesis was to define the effects of sludge characteristics on ash behavior. This includes the fly ash formation, volatilization of ash-forming species, bed agglomeration, ash deposit growth and trace element enrichment in the submicron particles and in the bottom ash. Although some of these phenomena take place downstream of the furnace, the environment studied is mainly the furnace. Ash behavior downstream of the furnace is highly dependent on several boiler-related factors, such as the boiler geometry, superheater temperatures or flue gas cleaning devices. Therefore, ash deposition on heat exchangers, tube corrosion and particulate emissions are not included here. Neither is the ash management and disposal discussed. These issues require special attention in future studies and probably results from this thesis can be used as background information.

Two sludge types were studied: paper mill sludges and a pulp mill sludge. The paper mills were modern integrated processes including thermomechanical pulping (TMP), paper making and deinking. The studied pulp mill was based on sulfate-process. Differences in the sludge composition were clear enabling us to define which problems would be typical in a pulp mill or in a paper mill. Field measurements in the paper mills included two different fluidization processes, a bubbling fluidized bed and a circulating fluidized bed. Because the sludges used were similar in both units and the operating conditions were alike, fruitful comparisons between these technologies could be made. The pulp mill sludge was fired both on an industrial and bench scale. This allowed us to study the effect of BFB scale-down on the ash formation and bed agglomeration.

Sludge ash behavior is a new research field with many questions, but only few answers. Several measurements described in this work are the first of their kind with these fuels, and are sometimes unique even when compared to studies with other fuels. Therefore the work has been empirical. The thesis is constructed so that the fate of the ash-forming species in the furnace can be followed from the parent sludge clump into an ash particle or the ash deposit formed in the bed or furnace wall. The publications are not followed in chronological order. This has allowed an overall presentation of the governing mechanisms. Also unpublished results obtained during this research are included to give more background for conclusions.

2. Literature review

2.1 Fluidization of powder systems

Fluidization is the operation by which solid particles are transformed into a fluid-like state through suspension in a gas or in a liquid (Kunii and Levenspiel, 1991). The fluidization of gas-solid systems is affected mainly by the gas velocity and powder quality. Powders have been grouped by Geldart (1986) according to their fluidization characteristics (Figure 1). Fluidization of particles less than 20 μm is difficult due to interparticle forces, which are larger than the fluid can exert. This cohesive powder type is called group C. Stickiness, porosity or electrical charges will increase the interparticle forces and deteriorate fluidization. The size range of aereable particles, called group A, is typically 20-100 μm depending on the density difference between the particle and the fluid. These powders have widely been studied due to their use in the catalytical cracking processes (e.g. Matsen, 1996 and Avidan, 1997). The sand-like powders are group B. They form bubbles when fluidized and they are used in combustion processes. The sand is typically 100-300 μm in the CFB, and 300-1,000 μm in the BFB. Group D is called spoutable, and the particle size is over 600-1,000 μm . Their mixing in fluidized beds is poor resulting in particle segregation. When coarse material is accumulated in the bed the fluidization becomes unstable. A remedy for this is to extract the coarsest bed material and replace it by fresh sand in the group B regime.

Fluidization stages with different gas velocities have been presented e.g. by Kunii and Levenspiel (1991). At low velocity the fluid will pass through the void space in a fixed bed of solids and no bed movement is observed. At certain pressure drop through the bed, the fluid upward force on particles will counterbalance the bed weight resulting in gas channeling and bubbling. This stage is called minimum fluidization and the corresponding fluid superficial velocity is the minimum fluidization velocity, U_{mf} . When the gas velocity is increased, the gas will form bubbles and result in bubbling fluidization. If the velocity is increased further the fluidization becomes turbulent and particles are entrained in the upward gas flow. The circulating fluidized bed is operated in this regime and the entrained particles are separated from the gas flow in a cyclone and recycled to the bed. Lean phase fluidization with pneumatic

transport takes place at the highest velocities. Between the turbulent fluidization and pneumatic transport is a separate fluidization phase called fast fluidization. Horio (1997) has described the shift from turbulent to fast fluidization as a state when the dense particle clusters become macroscopically fluidized.

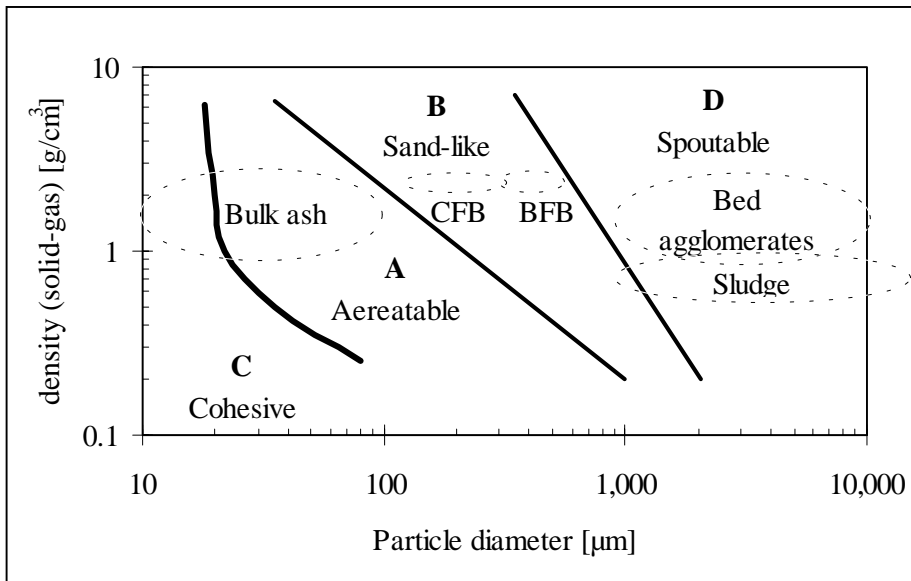


Figure 1. Particle characterization according to fluidization properties as defined by Geldart (1986). Approximate locations of bed materials used in fluidized bed combustors, sludge, sludge-derived ash and bed agglomerates are added.

2.2 Combustion in fluidized beds

The choice between the BFB and CFB combustor is made according to the fuel characteristics and economics. The unit size of the BFB is typically below 100 MW_{thermal}, while the CFB is less restricted by size. High-carbon fuels, i.e. coal, are mostly fired in the CFB. The char burnout in the CFB is higher than in the BFB, because the char particles can be separated from flue gases in the cyclone and conveyed back to furnace. For low-carbon fuels like wood and sludge, combustion efficiencies are high with both technologies. The high fluidization velocities in the CFB, 30-40 times U_{mf} or above, increase pressure losses in the air system and accordingly the power consumption. The fluidization velocity is

lower in the BFB, typically 4-5 times U_{mf} , and less power is needed. Hence, BFB units have certain economical advantages for firing low-carbon fuels. Problems in ash handling or ash deposit formation are important issues when choosing the technology. Unfortunately only limited information on these problems in sludge combustion is available. The in-furnace temperature profile can be assumed to be stable in the CFB. Deviations are as low as 30 °C (Brereton, 1997). The deviations are more pronounced in the BFB, especially in the freeboard, where the solid particle concentrations are relatively low.

Solid fuel combustion includes the following phases: i) heating of the fuel and drying of moisture, ii) pyrolytic devolatilization of the volatile organic material, iii) flaming combustion of the devolatilized compounds and iv) residual char combustion (Kanury, 1993). Efficient mixing of solids distributes fuel rapidly among the hot bed material and the contact between the fuel and the bed material transfers heat from the exothermic combustion reactions to the endothermic moisture vaporization and devolatilization. This results in a uniform bed temperature and enables the use of relatively low bed temperatures, which is one of the main advantages in the FBC. The typical operational temperature is 800-900°C to ensure complete char burnout, but seldom over 900 °C due to possible ash softening and bed agglomeration, especially when firing wood-based fuels. If limestone is used in the bed for sulfur removal, the optimum bed temperature is around 850 °C (Basu and Fraser, 1991, Bramer, 1995).

Fuel particle size, density, and the fixed carbon content (C_{fix}) are important factors in the FBC. Coal and sand densities are within the same range, hence small coal particles are easily distributed in the bed. The coal C_{fix} concentration is typically high and the glowing char combustion dominates the combustion reactions. This results in an even distribution of combustible material and heat release in the bed. Temperatures on the burning char particle surfaces are higher than the average bed temperatures. Recent studies with coal indicate that this difference is 20-200 °C (Winter et al., 1997). Tests with petroleum coke show similar results, 60-360 °C (Linjewile et al., 1994). The highest temperatures were observed in the bubble phase and close to the bed surface.

Sludge behaves differently. Sludge is less dense than sand and the particle size is larger. Wirsum and Fett (1997) showed that large bodies of the same density

as the bed suspension will float on the bed surface. It was stated that sludge particles tend to maintain their shape and do not easily fragment during the combustion. Studies on large particle movement by Pruden et al. (1975) showed that if the particle density is less than the sand bed suspension density, about $1,000 \text{ kg/m}^3$, the large particles floated on the bed surface. Correspondingly particles with a higher density sank. The sludge density is $1,000 \text{ kg/m}^3$ or below, hence these analyses also suggest that sludge is likely to float on the bed surface. Another difference compared with coal is the low C_{fix} concentration in the sludge. Tests in a bench-scale BFB with sewage sludge, the concentration of C_{fix} being 15 weight-%, indicated that the combustion was dominated by the burning of the volatilized organic compounds rather than char combustion (Ogada and Werther, 1996). The carbon content in the bed was low and the formed char was highly reactive. The sludge was fed into the bed bottom, but even so the combustion was concentrated on the bed surface. A test run with propane showed a similar temperature profile. Tests in a laboratory BFB with coal showed that the volatiles do not burn in the dense bed, but rather in bubbles or above the bed (Hayhurst and Lawrence, 1995). Evidently, both the flotsam nature of the sludge and the combustion of volatile organic species will concentrate the heat release on the bed surface.

A further difference between sludge and coal is that the combustion phases in the fuel particle are not similarly structured. Ogada and Werther (1996) stated that moisture vaporization, pyrolysis and char combustion overlapped significantly during the sewage sludge combustion. This resulted in lower temperatures in the sludge during the devolatilization stage than were measured e.g. in a burning wood particle. This was considered to be due to the cooling effect of the sludge moisture evaporating from the particle center through the burning surface layer. The highest measured peak temperatures were $200 \text{ }^\circ\text{C}$ above the bed temperature. Wirsum and Fett (1997) measured the total combustion time for 300 g sludge clumps to be 10 minutes. These results indicate that the time needed for moisture evaporation is probably much longer than that required for char combustion and evidently the drying phase will affect the sludge overall-combustion characters as showed by Ogada and Werther. The char formation was influenced as well by sludge moisture. When firing wet sludge, 79 % of the sludge-inherent carbon was released as volatiles, while for dried sludge it was 69 %. It was suggested that the evaporating steam resulted in the partial gasification of char in the wet sludge. An important factor in char is

how easily it will be fragmented. Chirone et al. (1991) formulated that during coal combustion in the BFB the carbon related phenomena are i) primary fragmentation, ii) secondary fragmentation, iii) fragmentation by uniform percolation and iv) attrition. Primary fragmentation is caused by thermal shock and internal stresses during devolatilization. Secondary fragmentation results from the weakening and breaking up of the char structure by combustion and collisions. Fragmentation due to uniform percolation takes place during the end of combustion when the pore size increases rapidly and the char structure collapses. Attrition is the release of fines from the particle surface due to wearing in the bed. The primary fragmentation is negligible for low-volatile fuels, like coke, due to the low devolatilization rate, and the secondary fragmentation prevails. Coals with a high swelling index are affected by the primary fragmentation. Uniform percolation and attrition create mainly fines. Fragmentation of high-carbon fuels is typically assisted by combustion. The formed char particles are coarse and dominate the combustion. Tests in a laboratory BFB indicated that this is not the case with a high-volatile fuel, such as wood. Here the char combustion proceeded via generation of fine char by attrition (Chirone et al., 1997). As described by Ogada and Werther (1996) the sludge-derived char is very reactive, which is directly related to high porosity. Therefore, the generation of char fines during sludge combustion can be expected to be high.

It can be concluded that the sludge combustion characteristics are different from conventional fuels like coal. Most likely this will also affect the ash formation. It is evident that the sludge combustion will take place on the bed surface, which will result in higher temperatures in the upper bed region than in the lower bed region. Another typical feature with sludge is that the heat release in the bed is mostly due to the combustion of volatile organic compounds rather than char combustion. Sludge is an unusual fuel due to its high moisture content. The moisture evaporation results in low combustion temperatures on the char surface, reduced char formation and overlapping of the char combustion with the moisture vaporization stage and pyrolysis. Neither is the final char combustion similar with sludge and coal. The char in sludge is most likely friable and will fragment into fines unlike the coals, which will derive larger char particles.

2.3 Ash formation during pulverized coal combustion

2.3.1 Ash-forming minerals

The best understanding of the ash-forming mechanisms originates from pulverized coal combustion research. Ash-forming species in coal have been grouped by Linak and Wendt (1993) and Sarofim and Helble (1993) into three categories: i) included minerals, ii) excluded minerals and iii) inherent minerals. The included minerals are inorganic entities within the fuel particle in a crystalline or glassy form. The excluded minerals consist of distinct and separate mineral particles. The inherent minerals are chemically bound in the organic structure. The included and excluded minerals are typically in supermicron size range and their chemical composition is refractory. Hence, these minerals form mainly supermicron residual ash particles via coalescence. The inherent minerals are atomically dispersed in the fuel structure and prone to be volatilized.

2.3.2 Formation of ultrafine particles

During pulverized coal combustion the flame temperature is high, 1,700 °C or above. In addition to the easily volatilized ash species like Na, As or Pb, some of the refractory metal oxides, namely SiO₂, CaO and MgO are volatilized, due to their decomposition via chemical reduction to more volatile suboxides or metals, SiO, Ca and Mg (Quann and Sarofim, 1982). These reducing conditions will exist in the boundary layer of the burning char particle. The volatilized fractions vary between different coals, and are higher in subbituminous coals and lignite, where the concentration of organically bound alkaline earth metals is higher, than in bituminous coals. Baxter et al. (1997) have stated that the convective forces during combustion can remove atomically dispersed refractory oxides from fuel into the gas phase. The vaporized refractory oxides nucleate forming about 10 nm primary particles (Helble, 1987). It has been suggested by Kauppinen et al. (1995) that outside the char boundary layer the particle size increases rapidly due to collision and coalescence with other primary particles. The final ultrafine particle mass mode is typically around 0.1 μm (Joutsensaari et al., 1993, Kauppinen et al., 1995). Species that require lower temperatures for condensation will do that on the surface of the existing particles formed via nucleation (Neville and Sarofim, 1982, Quann et al., 1990).

2.3.3 Residual ash formation

Ash species that are not volatilized during combustion, but remain in the solid combustion residue, form the residual ash. The residual ash particle growth during pulverized coal combustion has been described as a coalescence of mineral inclusions or addition of the atomically dispersed elements to existing particles on the char surface (Kang et al., 1990 and Kang, 1991). Coalescence has been found to be the primary ash formation mechanism e.g. by Helble et al. (1990). The char macroporosity is an essential variable controlling the formation process. The residual ash particle size is increased by the mineral coalescence, but the char fragmentation will decrease it by reducing the size of the parent char particles (Kang et al., 1990). In an extreme case a non-porous char will produce one ash particle from one fuel particle. Char is prone to fragment along the pores and consecutively limit the ash particle growth. Results with typical coals show that combustion of a single coal particle will result in 100-500 residual ash particles (Helble and Sarofim, 1989). Fragmentation occurs mostly during combustion and not during drying or volatilization. Erickson et al. (1992) have demonstrated in a drop-tube-furnace with a synthetic coal that close to one ash particle per coal particle was formed. Also they found that the increased fragmentation at higher temperatures resulted in higher numbers of ash particles.

These two main mechanisms of ash formation, fine particle formation via condensation and residual ash formation via mineral coalescence, result typically in a bimodal fly ash size distribution, where the first mode is in the submicron range and the other mode is supermicron (Quann and Sarofim, 1982, Quann et al., 1990). Gaseous species do not entirely end up in the fine particle mode, because heterogeneous condensation also transports material on the residual ash surfaces. Similarly chemical reactions incorporate gaseous species in both size modes. Enrichment of volatile species on residual ash surfaces by condensation has been reported e.g. during combustion of coal (Haynes et al., 1982, Gallagher et al., 1990) and municipal solid waste (Taylor et al., 1995). A schematic presentation of the ash-forming mechanisms has been given e.g. by Sarofim and Helble (1993).

2.4 Ash formation in the FBC

The ash-forming species have various pathways in FBC. i) The largest mineral particles, typically over 100-300 μm , remain in the bed and are extracted from the process with the bottom ash. Also ash particle attachment or vapor deposition on the bed material surface can accumulate ash species in the bottom ash. ii) Fly ash consists of particles entrained from the furnace by flue gases. This includes the residual ash particles, which typically are in the supermicron range, as well as the ultrafine particles formed by condensation. iii) Ash species might also be deposited on the furnace wall or heat exchangers via particle deposition, vapor condensation or chemical reaction. iv) Some inorganic species may remain in gas-phase at flue gas exit temperatures and do not participate in ash formation. This is namely true for SO_2 , HCl and some trace elements, e.g. Hg species.

Due to the low combustion temperatures in FBC the volatilized fraction of ash-forming species can be expected to be lower than during pulverized coal combustion. Measurements in CFB coal combustion indicated, indeed, that this is the case (Lind et al., 1996). The fly ash mass size distribution had only one mode locating in the supermicron range. On a number basis a submicron mode formed of condensed particles was observed at 0.02 μm , however, reduced in quantity by three orders of magnitude when compared to pulverized coal combustion.

Fuels in which the ash-forming species are bound in the organic structure are prone to produce volatilized ash also in FBC. This is evidently the case with many biomass fuels (Nordin, 1994). The plant metabolism requires cations in the form of e.g. alkali and earth alkali metal ions. The concentration of these species and in particular of K is highest in fast-growing plants, such as straw. Hence during biomass combustion the volatilization of ash-forming species should be more pronounced than with coal. This has also been detected in several experiments. During straw combustion in a grate-firing unit K, S and Cl species were volatilized (Christensen, 1995). When switch-grass was burned in a laboratory furnace at 800 $^{\circ}\text{C}$, gas-phase NaCl and KCl were formed (Dayton et al., 1995). Only limited information is as yet available on the ash-forming mechanism with wood fuels. The potassium concentration in wood is lower, about 0.1 %, than in grasses, 1.0 % (Miles et al., 1996). Nordin (1995 A)

reported even lower values for pure wood, 0.04 %. Therefore wood and bark are considered to be non-fouling fuels. However, recent results show that K, S and Cl species are volatilized during wood combustion in a CFB (Lind et al., 1997).

Melting of ash-forming species in FBC is harmful. Liquid species are likely to be attached onto the bed sand and cause bed agglomeration. In the freeboard the molten particles can initiate deposit formation. Obviously the molten species will be enriched in the bottom ash as demonstrated e.g. by Ho et al. (1994). Skrifvars and Hupa (1995) have described the ash behavior as a multicomponent eutectic compound. According to this method the ash melting does not occur at a certain temperature, but the fraction of the molten phase will increase linearly between the temperatures where the first melting occurs and when all material is molten. It is stated that low weight fractions of melt, 10 % or above, can make the ash sticky. However, for most ashes the thermodynamic data is not sufficiently accurate to allow calculation of these temperatures (Skrifvars et al., 1997).

Particle adhesion can also be an enrichment mechanism. Adhesion without material binding may occur due to surface forces, like van der Waals or electrostatic forces. They are inversely proportional to the square of the particle diameter ($\sim d_p^{-2}$), hence the smallest particles are most affected by these forces (Berbner and Löffler, 1994). When a material bridge is formed between the adhered particles, the binding forces increase significantly. Only limited information is available on these mechanisms in the FBC. It can be assumed that species which are bound in fine particles, or species that melt or increase sintering in the ash structure are prone to be attached to the bed material, combustor wall or heat exchangers.

Accumulation in the bed is counterbalanced by fragmentation and attrition. Shamlou et al. (1990) discovered in experiments with glass particles that attrition rather than fragmentation is the mechanism that generate fines in fluidized beds. Similar results have been shown by Mullier et al. (1991). This suggests that the ash species adhered to bed particles are prone to be fragmented by attrition. Correspondingly large and dense ash particles will probably maintain their shape without significant size reduction. Attrition in the BFB takes place either in the fluidization air entry region or in the bubbling bed. While several matters, like bubble flow pattern and air nozzle design are of importance,

there is evidence that attrition rates both in the bubbling bed and in the air distributor area are proportional to the excess gas velocity, $U-U_{mf}$ (Seville et al., 1992). In the CFB the attrition has been studied during char fragmentation. It has been proved by Arena et al. (1990) that the generation rate of char fines in the CFB is one order of magnitude higher than in the BFB.

Several factors described above suggest that a high number of ash particles will be formed during sludge combustion in the FBC. These include char fragmentation, high attritional forces and low combustion temperatures, which do not favor mineral coalescence and formation of dense and non-friable particles.

3. Methods

3.1 Physical and chemical analyses

A large variety of analyzing equipment were used during this research. The methods are described in each publication, and here their usefulness is shortly discussed. The standard method used to analyze the concentration of ash-forming species in fuel is to heat the fuel sample in an oven at 800 °C so that all combustible material is consumed. If ash-forming species are volatilized from the sample, the result is lower than the total concentration of inorganic species in the sludge. Therefore, for biomasses, lower temperatures such as 550 °C were used e.g. by Skrifvars et al. (1995). However, the question of defining what is a sufficiently low ashing temperature in general has not been resolved. In this study the ashing was carried out for paper mill sludges at 800 °C and for pulp mill sludges, where the concentration of volatile inorganic species was higher, at 500 °C.

Thermogravimetry (DTA/TGA) was used to observe the sludge combustion behavior and transformation of the residual ash at high temperatures. One result from these studies was that in paper mill sludges the inorganic species were not volatilized at measured temperatures less than 1,200 °C (Publication 1, Figure 7). This suggests that the ashing at 800 °C did not affect the results of sludge ash content. The bulk fly ash specific surface area was measurement by nitrogen adsorption (BET surface area). The BET-measurements could be compared to the fly ash surface area concentrations calculated from the aerosol measurements. This information was valuable, as the pathway of the volatile species into fly ash via condensation or chemical reactions was considered.

Ash chemical composition is typically measured with elemental analyses. In this study both X-ray fluorescence (XRF) and inductively coupled plasma spectroscopy (ICP) were used. The results in XRF were observed to be more reliable for the main elements. The advantage in XRF is that the samples are not dissolved unlike for ICP or atomic absorption spectroscopy (AAS). For ICP the sample was dissolved in a mixture of nitric acid and fluoric acid. Problems arise especially with silicate ashes due to their scarce dissolution, hence less reliable results for the main elements in the Si-based ashes may be obtained. However,

ICP and AAS are more sensitive to trace elements than XRF. Therefore, in this study the main elements were analyzed by XRF and trace elements by ICP using, in most cases, mass spectroscopy (ICP-MS). Results in Publication 2 were obtained by ICP atomic emission spectroscopy (ICP-AES), which is less sensitive to trace elements. Concentrations of water-soluble species in ash were analyzed by ion chromatography (IC). For detection of the condensed species in the impactor samples, which were mostly sulfates and chlorides, this method proved to be more reliable than the ICP-MS.

To detect crystalline species in the bulk samples, X-Ray diffraction (XRD) was used (Publications 1, 4 and 6). The sludge ash was highly amorphous and only main paper additive mineral phases were detected. Neither was the quantification of these results possible. Similar problems occurred with sludge samples due to their irregular fibrous structure.

3.2 Analyzing S and Cl in sludge

Paper mill sludges included high concentrations of ash-forming species and especially calcite, which is known to capture S and probably also Cl during combustion. This is a problem for fuel analyses, because they are based on detection of the combustion products in the gas phase. Standard analysis of S is performed by combusting the fuel sample in oxygen at 1,350 °C, successively detecting the formed SO₂ in flue gases and converting the concentration in the sample mass (ASTM D4239). In Cl analysis the fuel sample is combusted in oxygen in the presence of Na₂CO₃, which absorbs the released Cl. This absorbent is analyzed further to obtain the Cl content in the fuel (ASTM D4208). Both methods are based on the assumption that the residual ash does not capture the volatile species. With low-ash fuels this is quite likely the case, however, with ash-rich sludges the capture in residual ash will result in low detected concentrations. Therefore, a set of paper mill sludge samples was first analyzed with the standard methods, and the non-combustible ash residue remaining in the calorimeter was further analyzed in IC to obtain the residual S and Cl concentrations. Compositions of the paper mill sludges are presented in Publication 6.

The results are compiled in Figure 2 and they show that the standard methods detected, in the ash-rich sludge, about 80 % of S, but only 30-70 % of Cl. The molar ratio of Ca/S in the fuel correlated with the S capture. The Cl capture correlated best with the fuel ash content. The measured Cl concentrations were close to detection limits, increasing the probability of error. The standard analyses gave better results for low-ash sludge and wood fuels. According to these results the standard fuel analyses of S will show too low values due to capture in the residual ash if the Ca/S molar ratio is over 40. Error in the Cl analysis is probable for sludge samples containing more than 20-40 % ash. The pulp mill sludge contained higher mass fractions of S (Ca/S, 0.95) and Cl, and the standard analyses probably gave reliable results. A further conclusion is that some of S and Cl is captured in the ash during combustion. The high S capture in paper mill sludge ash during FBC combustion has been detected e.g. by Anthony et al. (1993) and Xiaodong et al. (1997).

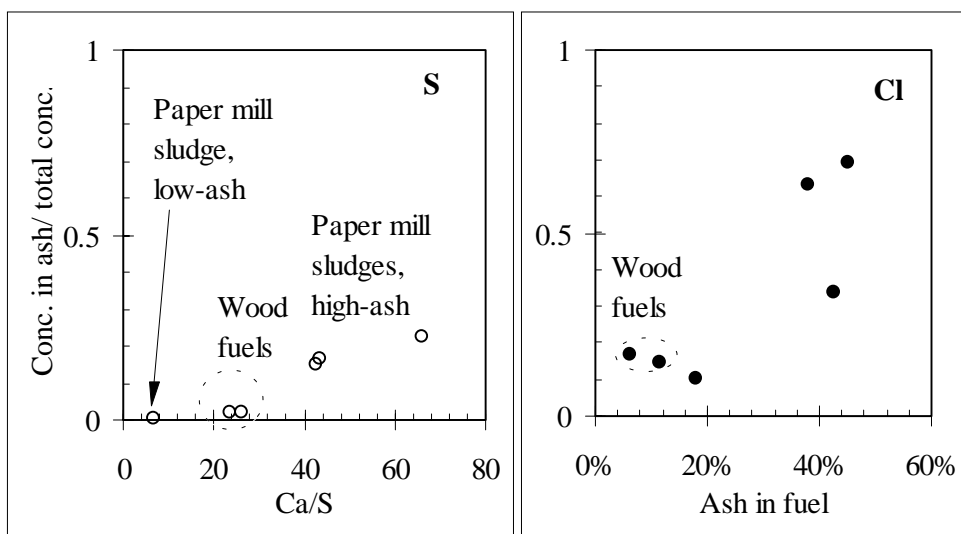


Figure 2. The fraction of sulfur and chlorine captured in residual ash during standard fuel analyses of paper mill sludges and wood fuels. Concentration from the IC-analyses divided by total concentrations (standard analyses and IC).

3.3 Aerosol measurements and microscopy work

To define the ash formation mechanisms in the submicron range, measurement techniques developed in aerosol science were used. Berner-type low pressure impactor (BLPI) was the basic tool used during this research. The advantage of BLPI is that practically the whole particle size range, above 0.01 μm , can be covered. Submicron particle concentrations can be measured on-line by the differential electrical mobility analyzer, DMA (scanning mobility particle sizer system, SMPS). However, in DMA the practical upper size range is 0.5 μm . An electrical low pressure impactor (ELPI) is also an on-line device and it covers the size range up to 5 μm . Tapered element oscillating microbalance (TEOM) was used to monitor the fly ash mass concentration below 5 μm range. The ELPI is a relatively new measurement device and comparisons to other equipment are scarce (Keskinen et al., 1992 and Moisio et al., 1995). Presently Publication 6 is the most elaborated study where all these techniques are simultaneously used in an industrial application and their results are thoroughly compared. More detailed discussion of aerosol measurement methods with the relevant references is given in this paper.

Scanning electron microscopy (SEM) was a fundamental research tool during this work. Typically, magnifications of 10,000 or above were needed to characterize the submicron particles. Therefore field emission (FE) high resolution SEM was applied (HR-SEM, Leo Gemini 982 DSM). A more detailed description is given in Publication 6. Low acceleration voltages, in the order of 1 kV in the HR-SEM, were essential when observing the morphology of submicron structures. Transmission electron microscopy (TEM) was used for the highest magnifications (Publication 4, Figure 4). The chemical composition of ash particle structures was qualitatively analyzed with electron dispersive spectroscopy (EDS, Noran Voyager Type 3.7) and quantitatively with wavelength dispersive spectroscopy (WDS), which has previously been used for ash analyses e.g. by Rink et al. (1995). Often WDS is referred to as electron probe microanalyzer (EPMA). WDS proved to give reliable results when the particle size was over 2 μm . Below that size the signal from the particle decreased and the background signal from the surrounding media increased. Also ash porosity caused problems. The WDS analyses converted to oxides yielded about 100 % in the solid particles, but only 60-80 % in the porous ones.

4. Sludge characteristics and ash formation in industrial fluidized bed combustors

4.1 Combustion properties and ash-forming species

The combustion of wet material, e.g. wood fuels, can be sustained in FBC when the adiabatic combustion temperature is 1,050-1,100 °C or above, (McCann., 1997, Louhimo, 1993). These values were 1,174-1,223 °C in the industrial BFB and the CFB firing paper mill sludge and wood fuels (Publication 6, Table 1). Using the fuel analyses of the paper mill sludge and wood co-fired in the pilot BFB, the calculated values were 1,500 °C or above (estimations based on Publication 2, Tables 1 and 4). Part of the volatile combustibles were burned with secondary air in the freeboard, where the temperatures were about 300 °C above the bed temperature. Combustion efficiency loss as CO in the furnace exit was negligible, 100-1,000 ppm with 3-5 % excess oxygen. Unburnt in the fly ash was below the detection limit and the reactor was insulated, hence the bed and furnace temperatures could be used for an estimation of the fuel heat release in the bed. These calculations indicate that 52 % of the fuel heat was released in the bed (primary/secondary air 70/30, fuel moisture 40 %, temperature in the bed 800 °C and in the furnace 1,100 °C). Volatiles accounted for about 90 % of the heat released from the sludge and wood mixture, hence, assuming that all the char was burned in the bed, 76 % of the heat released in the bed was due to the combustion of volatiles. These findings are consistent with the results of Ogada and Werther (1996), who indicated that the combustion of organic volatiles dominated the heat release in the bed.

The heat value of wet pulp and paper mill sludge is often less than is needed to support combustion. This is due to the high content of moisture and ash-forming species in the sludge. The combustible part in the paper mill sludge is composed of wood fibers, hence the heat value of the water and ash free fuel is similar to wood (Publication 4, Table 1). Correspondingly the ignition and combustion temperatures of the sludge measured in a thermogravimetry were close to the values of wood and paper (Publication 1, Figure 3). The volatiles burned at 230-350 °C and residual char at 380-470 °C. Not surprisingly, the main heat release took place when the volatiles were burned. The char was consumed at relatively

low temperatures suggesting that the char is very reactive. Reference test runs with low-ash newsprint and tissue paper samples did not produce residual char, but for high-ash glossy paper the char combustion was observed at 400-440 °C (Publication 1, Figure 3). Presumably, the high concentration of ash-forming minerals in the paper mill sludge was connected to the char formation. It is possible that the coating minerals on the fiber surface limited the diffusion of oxygen into the fibers and enhanced the formation of residual char under substoichiometric conditions. The heat value in the pulp mill sludge was lower than in the paper mill sludge due to the high moisture content, 85.7%. Also the heat value of ash and water-free sludge was lower than in typical wood fuels, showing that the combustible part in the sludge was not comparable to wood fibers (Publication 7, Table 1).

Table 1. Mass fraction of residual char in bed (Publications 2 and 4-7).

Combustor	Fuel	LOI, %	C, %
BFB, industrial	Paper mill sludge and bark		0.1
CFB, industrial	Paper mill sludge and wood waste		0.1
BFB, pilot-scale	Paper mill sludge and wood	0.1	
BFB, industrial	Pulp mill sludge and bark	1.4	0.3
BFB, bench-scale	Pulp mill sludge		0.04
BFB, bench-scale	Bark briquettes		0.1
BFB, bench-scale ¹	Sewage sludge		0.01
BFB, bench-scale ¹	Bituminous coal		1.8
BFB, bench-scale ¹	Graphite		37.1

LOI = Loss of Ignition analyzed by heating at 1000 °C in air

C = Sample burned in oxygen and analyzed by IR-detection

¹ Ogada and Werther, 1996

The measured carbon concentrations in the bed during pulp and paper mill sludge firing were low (Table 1), corresponding to the results from sewage sludge combustion (Ogada and Werther, 1996). The values for coal firing are much higher, especially for the non-volatile graphite. Using the fuel feed rate, fuel C_{fix} content and bed mass, it can be estimated that during the combustion of sludge and wood mixture an average residence time of a residual char particle in

the bed is less than one minute. This is a short time when compared to the previous measurements of the total sludge particle combustion time and confirms the suggestions that the char combustion is not the dominating combustion phase during sludge combustion.

Results in this study showed that the ash in paper mill sludges is formed of refractory paper additive minerals, kaolinite (clay), calcite and talc (Publications 1 and 6). Correspondingly the mass fraction of Si, Al, Mg and Ca species in the elemental analyses was about 90 %. The mass fractions of volatile species were low; in the sludge S was 0.1 % and Cl less than 0.1 %, and in the ashed sludge Na species represented 0.2-0.6 % and K species 0.2-0.9 %. Thermogravimetric analyses up to 1,200 °C did not show ash melting or volatilization, and sintering was initiated at 1,050 °C (Publication 1, Figure 7). Ash from another paper mill sludge was softened in a standard ash fusion test at 1,150 °C and the fluid temperature was 1,290 °C (Publication 4, Table 3). These values are clearly above the typical FBC temperatures of 800-900 °C. Crystalline phase analyses in XRD detected the paper additive minerals in the paper mill sludge samples ashed at 500 °C, but not at 900 °C and 1,050 °C (Publication 1, Table 4). Correspondingly, the formation of clay-based mullite and Al-Si spinel was observed at 900 °C and 1,050 °C. Calcium carbonate was transformed into calcium oxide in the thermogravimetric analyses in air at 550-630 °C. In flue gas, including CO₂, the oxidation takes place at higher temperatures and the fly ashes typically include unreacted calcite suggesting that the oxidation has not been complete (publication 6, table 6). Sulfur capture in atmospheric units is described as sulfation of CaO, but direct sulfation of CaCO₃ is also possible, especially at pressurized units (Anthony and Preto, 1995). The ash-forming minerals were observed in SEM on the surface of sludge fibers (Publication 1, Figure 1 and Publication 4, Figure 1). The minerals formed irregular clumps and the observed primary particle size in the clumps was in the micron-size range. This is similar to the size of paper additives. A typical mass mean size of the ash-forming minerals varies from fine coating clay, 0.5 μm, to coarser filler clay, 3 μm (Kouris and Kocurek, 1990). Crystalline phase analyses were not performed for the pulp mill sludge. The elementary analyses showed that Si, Ca and Mg were the main elements, their oxides comprised 68.6 % of the ashed sludge (Publication 7, Table 2). The mass fractions of volatile species were higher than in the paper mill sludge, S 1.1 % and Cl 0.6 %, and in the sludge

ashed at 500 °C Na represented 3.0 % and K 1.3 %. Also the mass fractions of Fe, 1.5 %, and Mn, 3.2 %, in the ashed sludge were considerable.

4.2 Fly ash formation

4.2.1 Residual ash particles

Fly ash was the most important ash type in the studied combustors. Fly ash made up about 90 weight-% of the ash-forming species during paper mill sludge combustion in the BFB and more than 95 % in the CFB (Publication 6, Table 1). During pulp mill sludge and bark co-combustion in the BFB the value was over 90 %. Fly ashes were in the supermicron range during paper mill sludge and wood fuel co-firing in the BFB by 97.3 weight-% and by 96.6 % in the CFB (Publications 6, Table 7). When pulp mill sludge and bark was co-fired in the BFB this value was 93.6-93.9 % (Publications 7, in-duct measurements). The remaining ash species were transformed in the bottom ash. In the BFB units the coarsest fly ash particles were collected from the flue gas duct and contained a minor fraction of sand (Publication 6, Table 4). These particles are not considered here as a separate ash type, but rather as large fly ash particles collected from the flue gases before an electrostatic precipitator (ESP). The coarse fly ash was circulated back to the furnace to enhance the bed fluidization in the BFB co-firing paper mill sludge and bark. Hence these particles, known as circulating ash, remained in the furnace longer than the average fly ash, resulting in particle densification and more pronounced formation of silicate compounds. Fly ash did not accumulate in the flue gas ducts in the studied CFB, presumably due to a smaller fly ash aerodynamic particle size.

The fly ash was mainly formed of sintered mineral particles (Publications 1, 4, 6 and 7). These particles were irregular in shape and porous, being similar to the mineral clumps observed in the parent sludge. This suggests that the mineral particle sintering takes place directly on the surface of the combustible fibers, resulting in a skeleton-type ash structure (Publication 4, Figures 1 and 2). Fly ash particle size was much larger than the additive clay minerals (Figure 3). The coarsest fly ash was sampled from the unit where paper mill sludge was fired in an air suspension with natural gas (Publication 3). SEM analyses showed that these particles were dense and more sintered than samples from the fluidized

bed combustors. Presumably, the higher temperatures in the gas suspension flame, the measured maximum temperatures were 1,300 °C, resulted in a less friable ash structure and larger particle size. Higher attrition rates in the FBC probably reduced the particle size as well. Another indication of the attrition was that the particle size in the BFB was larger than in the CFB. As discussed previously the attrition rates are higher in the CFB and probably this is the reason for the lower particle size in the CFB. It is also possible that the combustion temperatures especially in the freeboard are higher in the BFB, which can result in dense and less friable ash structure.

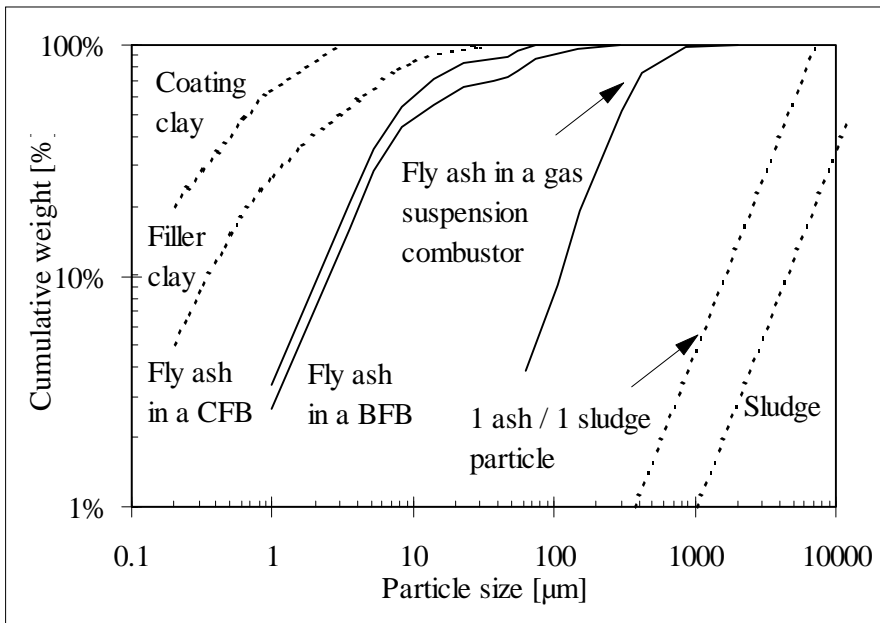


Figure 3. Measured fly ash size distributions during paper mill sludge combustion. Paper additive mineral size (Kouris and Kocurek, 1990), estimations of the sludge particle size and the maximum residual ash particle size are added.

Approximate calculations indicate that in FBC one fly ash particle contained in the range of 50-500 clay particles (Table 2). In a suspension combustor the result was 10^6 - 10^7 . Wet sludge does not have a measurable particle size., hence 10 mm is used as the mass mean size based on the observation that dried sludge forms 1-20 mm clumps. The results indicate that one sludge particle contains 10^9 - 10^{10} clay particles. This is several orders of magnitude higher than in the fly

ashes. It is difficult to estimate the margin of error, but one sludge particle produces possibly as many as 10^6 - 10^8 fly ash particles in a FBC. The number is much lower, 10^2 - 10^4 , for the suspension combustor.

Table 2. Calculated estimations of the number of mineral particle inclusions in an average fly ash particle during paper mill sludge combustion. Spherical geometry is assumed.

	<i>Particle mass mean size, μm</i>	<i>Clay particles in one ash particle,</i>
Clay, average (Kouris and Kocurek, 1990).	1.5	1
Ash particle porosity (estimate)	0.5	
CFB, fly ash (Publication 6)	7.5	63
BFB, fly ash (Publication 6)	12	256
Suspension combustion, (unpublished)	300	4.0E+06
Sludge particle size (estimate)	10,000	
Ash in sludge, weight-% (measured)	40%	
Dry sludge density, kg/m^3 (estimate)	300	
Clay density, kg/m^3	2,500	
One ash particle from a sludge clump	3,634	7.1 E+9

4.2.2 Mineral transformations in ash

Mineral transformations in ashes were studied by analyzing the ash crystalline structure in the XRD. The minerals that were detected in the paper mill sludge samples ashed at 500 °C were mostly transformed into amorphous phases and calcium and potassium silicates in the BFB fly ash. Indications of the paper additive minerals in the fly ash had almost disappeared (Publication 6, Table 6). The silicate formation had proceeded further and the original mineral structure had disappeared in the coarse ash particles, which were circulated back to the bed. Evidently, this was due to the longer residence time in the bed, indicating that the silicate formation was a time-dependent reaction. Similar silicate formation was observed in the CFB. The minerals were clearly detected in the fly ash, but not in the circulating bed, where instead a calcium silicate was

observed. The fraction of silicate in the fly ash was minor in the CFB, probably due to lower combustion temperatures than in the BFB. It is also possible that the fly ash residence time in the CFB furnace is shorter due to the fast circulation of solids, and this will result in less reacted ash. These results suggest that the transformation reactions in the paper mill sludge minerals are time-dependent. Another finding is that Ca species especially were observed to form silicates. The formation of calcium silicates from CaO-rich species and kaolinite has also been observed during pulverized coal combustion by Zygarlicke et al. (1990).

The main feature of the FBC fly ashes was their sintered and irregular shape. However, some spherical supermicron particles were also observed, suggesting that they were melted or fused during the combustion. These particles were always small, less than 20 μm and in most cases around one micron. This suggests that either the small particle size, sintering rates being faster in smaller particles, differences in particle residence time in the burning char according to particle size, or heat transfer limitation in the largest particles were the reasons for the higher degree of fusion in the smallest particles. The faster transformation of the smallest particles has been reported e.g. by Raask (1969) during experiments in a drop furnace with synthetic $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glasses. The fusion into spherical particles occurred at lower temperatures once the particle size was less than 50 μm . The difference in the fusion temperature between the 10 μm and 50 μm particles was 200 $^\circ\text{C}$. Assuming that this is valid also in the paper mill sludge, the bulk ash fluid temperature being 1,290 $^\circ\text{C}$, it can be estimated that a 10 μm particle will fuse at about 1,100 $^\circ\text{C}$. This is higher than the average bed temperature, but probably the peak temperatures in the burning char are sufficient for the particle fusion. The occurrence of spherical particles was low and no agglomerates formed of molten ash was observed. This is a further indication that ash fusion took place only in extreme conditions, probably on the burning char surface and the particles were solidified rapidly after leaving the combustion layer and did not initiate agglomerate growth.

The mineral transformations within ash particles are studied in Figure 4. It presents particle compositions in a ternary diagram, based on WDS analyses of fly ash particle cross-sections collected from the pilot BFB firing paper mill sludge. The chemical phases in the diagram (SiO_2 , Al_2O_3 and CaO) contained about 90 % of the ash-forming species. The high concentration of kaolinite is

visible in the bulk analyses of the ashed sludge. Calcite shifts the bulk analyses slightly towards the CaO corner. Analyses of the non-fused particles were scattered around the bulk analyses. These particles formed the major mass fraction in the fly ash, hence their concentration around the bulk analyses is understandable. None of the analyzed particles was of pure kaolinite or calcite, and all the main elements were always detected in the particle structure. Apparently sintering bound unselectively all types of minerals in the formed particles. The number of analyzed non-fused particles in this sample was only 7, but analyses of other samples were similar, containing in the order of 100 particles.

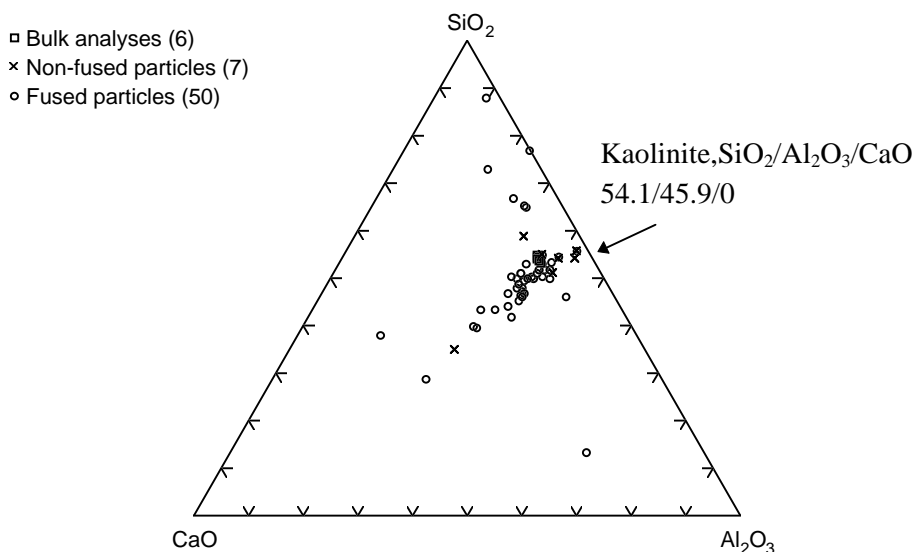


Figure 4. Supermicron fly ash particle compositions based on WDS analyses. Combustion of paper mill sludge in a pilot BFB (PDS1, Publication 2). Number of analyses are in parenthesis.

The fused particles showed a tendency to include higher Ca-concentrations than the bulk ash. Ca is known to act in the silicate system as a fluxing agent, decreasing the ash viscosity and fusion temperatures. Therefore, it is understandable that particles containing higher concentrations of Ca will be fused at lower temperatures than an average ash particle. However, a high concentration of Ca was not necessarily needed for the ash fusion. Hence, other

factors, like the location of ash particle in the burning char or the particle size, may result in particle fusion.

4.2.3 Ultrafine particle formation

One of the major findings in this research was that the fly ash in the FBC when co-firing paper mill sludge and wood fuels, included negligible mass concentrations of ultrafine particles. The fly ash mass size distributions were virtually unimodal. Of all ash-forming species only 0.3 weight-% in the BFB and 0.2 weight-% in the CFB was detected below 0.2 μm size (Publications 6, Table 7). On a number basis an ultrafine particle mode was detected in the BFB at 0.05 μm . The mode was less significant in the CFB. The submicron particles were mainly fragmented material from larger mineral particles (Publication 6, Figures 8 and 9). Assuming that vapors were not absorbed entirely into the porous bulk ash, it is concluded that the volatilized fraction of the ash-forming species was low.

The situation was different during pulp mill sludge and bark co-combustion in the industrial BFB, where the volatilization of ash-forming species was clearly detected (Publication 7). Fly ash mass size distribution was bimodal and the ultrafine particle mode consisted of spherical particles formed via condensation, and their agglomerates formed via collisions, including 2.2-5.0 weight-% of fly ash. The ultrafine ash was water-soluble and about 80 weight-% of this material consisted of K^+ and SO_4^{2-} the rest being Cl^- and Na^+ . Presumably, the higher concentrations of Cl, 0.6 weight-%, and S, 1.1 % in the pulp mill sludge than in the paper mill sludge (Cl <0.1 % and S 0.2-0.9 %) enhanced the volatilization. Especially Cl has been found to increase the volatilization of alkali species, e.g. Olsson et al. (1997) detected this during laboratory tests with wheat straw.

Mass fraction at the 0.3-1 μm range was low during the tests with pulp mill sludge, 1.2-1.4 %. Similarly low concentrations were observed with paper mill sludge at 0.2-1 μm , 2.4 % in the BFB and 3.2 % in the CFB. Evidently, with both sludge types the fraction of fragmented submicron particles was low. This suggests that the mineral particles in sludge are efficiently captured in the sintered ash. Neither is the ash fragmentation into fine particles excessive. The higher mass fraction of the fragmented submicron particles in the CFB than in the BFB during paper mill sludge firing are consistent with the fact that the attrition rates in the CFB are higher.

4.2.4 Heterogeneous condensation

Even though the mass fraction of particles formed via condensation during paper mill sludge firing was negligible, it is possible that some species were volatilized and captured on fly ash surfaces via heterogeneous condensation. Particle diameter growth rate is inversely proportional to particle diameter, when the particle size is above the gas mean free path (Hinds, 1982). In the case of smaller particles the diameter growth rate is independent of size due to Kelvin effect. The gas mean free path in boiler conditions ($T = 500\text{-}1,000\text{ }^{\circ}\text{C}$) is about $0.1\text{-}0.2\text{ }\mu\text{m}$. Therefore, by assuming a spherical particle geometry, the concentration of condensed elements in ash is $\sim 1/D_p$ (surface area divided by volume) for particles below that size and $\sim 1/D_p^2$ for larger particles. In both cases the concentration of condensed species should be highest in the smallest particles. Assumption of the spherical geometry is probably valid for the particles formed via condensation, but most of the residual ash particles were fragmented and irregular in shape. Similarly in the supermicron range the particles were rarely spherical or had smooth surfaces. This resulted in high fly ash specific surface area concentrations measured by BET, being about 300 times higher than that measured in the ultrafine particles during the paper mill sludge combustion in the BFB (Table 3). This ratio was about 10 in the BFB co-firing pulp mill sludge and bark. The BET-value was highest in this unit due to the elevated char concentration in the fly ash, about 14 %, and evidently the char porosity influenced the results. Otherwise, the BET value of low-char bulk ash varied between $7\text{-}10\text{ m}^2/\text{g}$, which is significantly higher than e.g. the value of limestone used for desulfuration $1.3\text{ m}^2/\text{g}$ (Iribarne et al., 1997). Fly ash BET-value in the bench-scale unit firing pulp mill sludge was $8\text{ m}^2/\text{g}$.

The extent of heterogeneous condensation is illustrated in the mass size distributions of K, Na, S and Cl in fly ashes in Figure 5. The graph indicates that the concentrations are, indeed, higher in the submicron particles. This is especially true for K during the pulp mill sludge firing, where the concentration increase is almost inversely proportional to the particle size. During the paper mill sludge and bark co-firing the increase is less pronounced. The same is true for the concentrations of Na, S and Cl in all samples. The higher concentrations in the submicron size suggest that at least part of these species were also volatilized during the paper mill sludge and bark co-firing.

Table 3. Calculations of specific surface areas in fly ashes. Comparison between bulk analyses and concentrations in ultrafine particles.

Bulk fly ash		A.	B.	C.	D.
Measured fly ash particle mass mean size	µm	12	7.5	15	24
Weight fraction of char	%	<1	<1	14.1	n.a.
Fly ash mass concentration in flue gas	g/Nm ³	4.49	8.28	1.12	1.06
Measured specific surface area in fly ash (BET)	m ² /g	7	10	27	8
Fly ash surface concentration in flue gases	m ² /Nm ³	31	83	30	8
Calculated equivalent primary particle size in fly ash *	µm	0.34	0.24	0.09	0.30
Ultrafine particles in fly ash					
Surface area concentration <0.2 µm determined by SMPS	m ² /Nm ³	0.1	<0.1 [#]		
Mass mean size <0.3 µm determined by BLPI	µm			0.1	0.1
Mass concentration <0.3 µm determined by BLPI	g/Nm ³			0.1	0.006
Calculated surface area conc. <0.3 µm determined by BLPI	m ² /Nm ³			2.6	0.2

A. Industrial BFB, paper mill sludge and bark firing.

B. Industrial CFB, paper mill sludge and waste wood firing.

C. Industrial BFB, pulp mill sludge and bark firing.

D. Bench-scale BFB, wet pulp mill sludge firing.

* A monodispersed spherical particle size with equivalent surface area / mass concentration as measured by BET.

Based on ELPI-measurements indicating lower ultrafine particle concentrations in B than A (Publication 6, Figure 6).

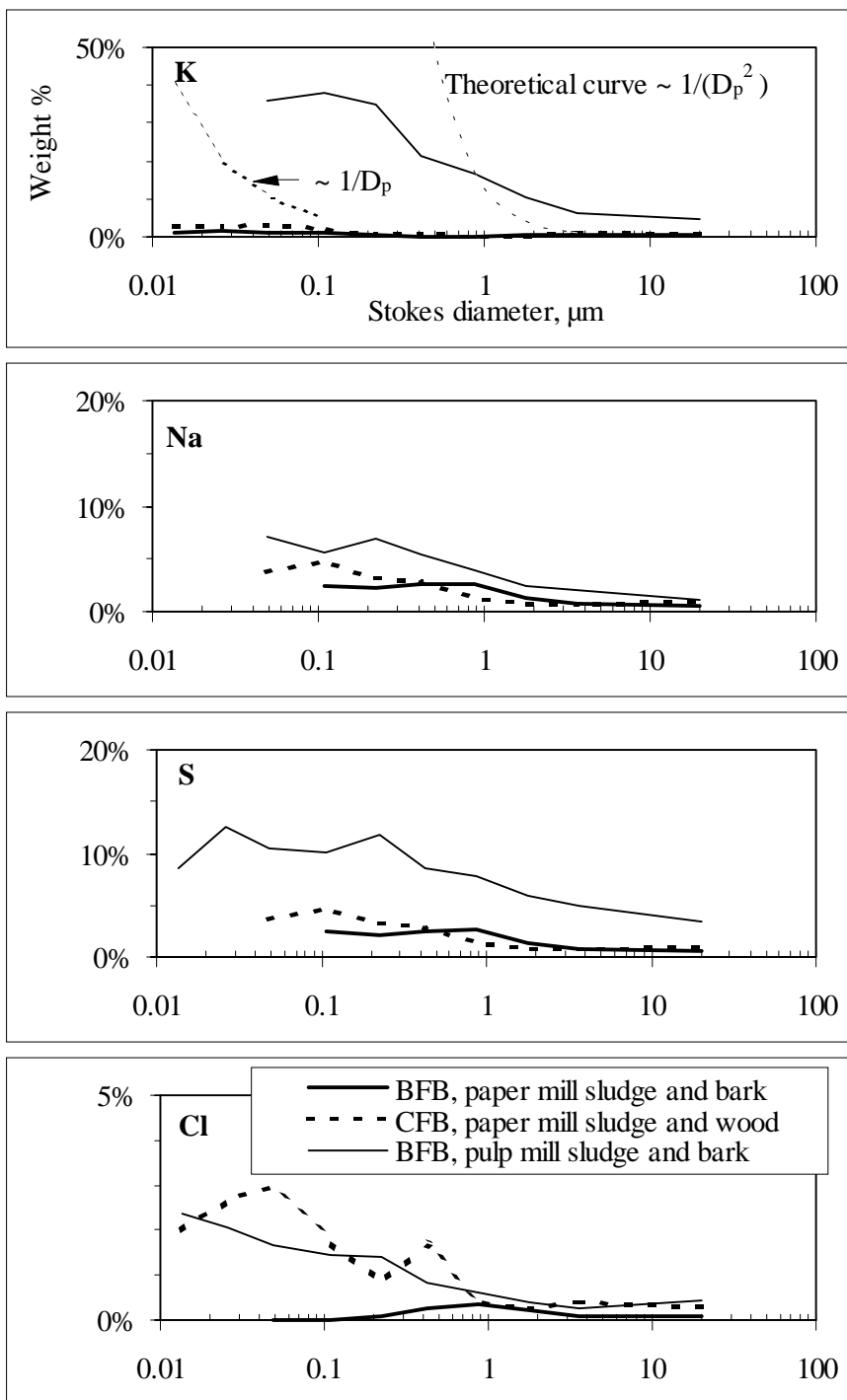


Figure 5. Volatile species concentrations in fly ashes (IC and ICP-MS).

Previous results showed that the condensation of ash species does not follow $\sim 1/D_p$ or $\sim 1/D_p^2$ as assumed when the particle sphericity is used. Three reasons for this behavior can be presented. Firstly, it is possible that only a small fraction of these species were volatilized during combustion. This has been discussed previously in the case of S and Cl capture in the paper mill sludge ash. It is known that kaolinite is prone to form silicates with alkalis, which was also detected in the ash samples from the BFB co-firing paper mill sludge and bark. Secondly, the high surface area concentration in the bulk ash probably creates a situation where heterogeneous condensation is quite insensitive to the particle size. Estimations presented in Table 3 support this suggestion. The third reason could be that capture mechanisms other than condensation are affecting the gaseous species. The flat concentration curves of S and Cl, when compared to K, during pulp mill sludge firing indicate this. Here especially the chemical reactions, e.g. with Ca species, are of concern.

4.2.5 Chemical reactions

The formation of CaSO_4 from gaseous SO_2 and solid CaO is a good example of chemical reaction between gaseous and solid phases. As described e.g. by Brereton (1997), the sulfation is dependent of the availability of reactive surface area in the CaO particle, therefore small particles are sulfated more uniformly than larger ones. Again the problem is understanding the effect an irregular particle shape has on the reaction rates. As discussed above, the assumption of spherical ash particle geometry is probably misleading.

Figure 6 illustrates the extent of chemical reaction between gaseous species and fly ash. Here the concentration of water-soluble Ca^{2+} is compared to the total concentration of Ca. Calcium species were not volatilized, and, in the form of carbonates or oxides, they are neither prone to dissolve in water. On the other hand, calcium sulfates and chlorides are water-soluble. Hence, the fraction of Ca^{2+} of the total Ca indicates how much of the available Ca has reacted with S and Cl.

These results show that chemical reactions do partly explain why the volatile species are found in high concentrations in the bulk ash. In the submicron size 50-100 % of the calcium has reacted with sulfur or chlorine. The fraction is 25-50 % in the 2 μm particles, falling below 10 % in the bulk ash. However, more than 93

weight-% of ash is in supermicron particles, hence most of the reactions take place in this size range. The decline in concentration towards larger particles is neither as steep as when assuming the proportionality to $\sim 1/D_p$. Evidently, the high surface area in the bulk ash enhances the reaction rates in all particle sizes. Another finding is the similar shape of the Ca^{2+}/Ca distribution curves in the different combustors. Even during paper mill sludge firing, when the concentrations of S and Cl were low, 50-100 % of the available Ca in the submicron particles had reacted. This indicates that reactions with gas-phase species are especially important in the smallest particles.

It can be concluded that the volatilized inorganic species are being captured in the large ash particles both by condensation and chemical reactions. Most likely this is due to the high surface area concentration in the bulk ash. It is also possible that some of the volatilized species are captured on the ash surface already within the burning particle, hence these species are not liberated in the flue gases. These findings suggest that the fraction of volatilized species is higher than the fraction of ultrafine particles in fly ash. However, a higher concentration of ultrafine particles is an indication of increased inorganic species volatilization, as was observed in the results from pulp mill sludge combustion.

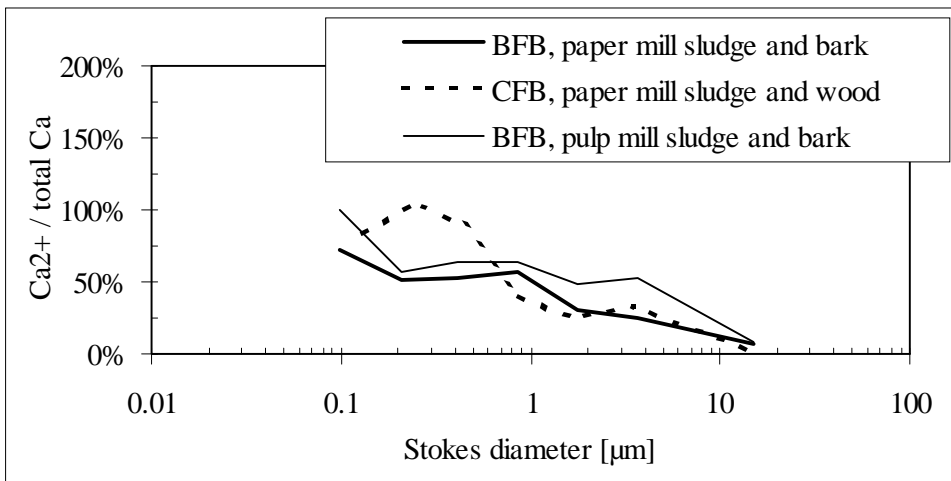


Figure 6. Concentration of water-soluble Ca^{2+} (IC results) divided by total Ca in fly ashes (ICP-MS and XRF results).

4.2.6 The fate of sulfur in fly ash

Sulfur is of special interest because it can either participate in the ash formation or remain as gaseous SO₂. Table 4 compiles the bulk ash analyses and the measured SO₂ concentrations in flue gases in the industrial BFB units. All the results consistently show that 85-89 % of S is captured in the fly ash. Evidently, the high Ca/S ratio in the sludges enhanced the capture by chemical reaction. This ratio was 19 in the paper mill sludge and bark mixture, and 6 in the blend of pulp mill sludge and bark. Presumably, the high surface areas in the fly ash also increased the capture by chemical reaction or condensation as discussed previously. Correspondingly the measured SO₂ concentrations were low. Results in the bench-scale BFB firing pulp mill sludge indicated similarly efficient sulfur capture. Higher bed temperature was not observed to increase the SO₂ concentration in the flue gases. However, higher bed temperature augmented the concentration of sulfur and alkali metals in the ultrafine size (Publication 7, Figure 5). The temperature insensitivity of S capture has also been observed by Xiaodong et al. (1997) when firing paper mill sludge in a pilot CFB.

Table 4. Fate of sulfur in the industrial BFB's.

Fuel		Paper mill sludge and bark	Pulp mill sludge and bark	Bark
Ash concentration	weight-%	17.7	3.1	2.3
Sulfur concentration	weight-%	0.07	0.11	0.03
S of ash-forming species	weight-%	0.4	3.5	1.3
S in fly ash	weight-%	0.5	3.4	n.a
Max. SO ₂ in flue gases	mg/Nm ³	214	131	70
Measured values	mg/Nm ³	26	19	8
Sulfur capture in fly ash		88 %	85 %	89 %
Ca/S molar ratio		18.9	6.1	22.7

Cl can also be considered to be an ash-forming agent or a gaseous pollutant in the form of HCl. Measurements of HCl were not available during these studies, hence definitive capture efficiencies cannot be calculated. However, as described

previously, Cl was present both in the fly ash submicron and supermicron modes, and Cl concentrations in the fly ash corresponded to the values of the ashed sludge samples (Publication 6, Table 4, Publication 7, Table 2). Evidently, a significant part of Cl was captured in the fly ash. Measurements in the bench-scale BFB firing pulp mill sludge indicated that an increased bed temperature did not affect the chlorine enrichment in the ultrafine ash (Publication 7, Figure 5). This suggests that Cl had already been volatilized at a lower temperature, and temperature increase had virtually no effect on the Cl capture. Xiadong et al. (1997) measured a low HCl concentration of 1 ppm during paper mill sludge combustion in FBC. Neither did they detect a significant increase in HCl concentration due to a temperature increase. In their studies with limestone Liang et al. (1991) found that Cl capture in Ca-species was negligible at bed temperatures much above 850 °C. Hence, the Cl capture in fly ash probably takes place at lower flue gas temperatures downstream of the furnace.

4.3 Bottom ash formation

The ash-forming elements made up about 10-15 weight-% of the bottom ash in the BFB co-firing paper mill sludge and bark (Publication 6, Table 4). During pulp mill sludge and bark co-combustion in the BFB the result was similar (Publication 7, Table 2). The sludge minerals were observed to remain amongst the bed material in two forms. The first form was large ash particles, which evidently were too large to be entrained from the bed by flue gases. Their chemical composition was similar to bulk ash and their morphology suggested that they were unfragmented residual ash particles. They were not observed to agglomerate with other ash particles or sand, neither were molten or condensed species detected on their surface. Obviously these particles remained in the bed as inert material. The other bottom ash type was an ash layer on the sand surface composed of micron-size particles, being rich in calcium (Publication 4, Figure 6, and Publication 7, Figures 6-8). During pulp mill sludge and bark co-combustion the sand surface was also observed to react with the calcium species, forming a silicate layer. The ash layer was porous and no molten or condensed species were detected in the layer.

While the accumulation of large particles in the bed is understandable, the ash layer formation raises many questions. Only limited information is available on

the ash adhesion mechanisms in fluidized beds. Layer growth on the sand surface during coal firing in a CFB has been reported e.g. by Manzoori and Agarwal (1993). It was suggested that the reason could be the deposition of alkali sulfates, which decreased the ash melting temperature and increased the ash stickiness and resulted in the layer formation. The layer growth was only slightly related to the bed temperature, indicating that physical processes rather than chemical reactions were the reason for ash deposition. Bénoni et al. (1994) discovered in their tests with sand particles that a decreasing particle size correlated with an increased agglomeration tendency in the bed. Calculations indicated that the fraction of the agglomerated 30 μm particles was 90 %, 60 μm particles 50 % and 100 μm less than 10 %. The particle attachment on the bed material surface has also been studied during filtration of fine particles e.g. by Ghadiri et al. (1993). These results suggested that for 1 μm particles the filtration efficiency was related to particle collection rather than retention. Once attached these particles did not re-entrain. For larger particles some retention aid, e.g. liquid film on the bed particle, was needed. Tests with clean sand showed low grade efficiencies for larger particles, but the grade efficiency was increased with a sticky layer, presumably due to their higher kinetic energy and penetration into the sticky layer.

Results in this study confirm that the small particle size is evidently one reason for the layer growth. As discussed previously, the measured fractions of 0.3-1 μm particles in the fly ashes were low. One explanation for this could be that these particles are efficiently adhered to the sand surface. A liquid layer was not observed on the bed particle surfaces, and attachment was presumably not assisted by a sticky layer, therefore only the smallest particles adhered. Hence surface forces, e.g. van der/Waals or electrostatic forces, may be the adhesion mechanism. Briens et al. (1992) discovered in their experiments with sand particles that electrostatic forces were not responsible for the agglomeration of fines. This leaves us with the suggestion that van der/Waals forces are the primary reason for adhesion. The possibility of adhesion by chemical binding cannot be neglected, but neither do we have any evidence of this. The enrichment of Ca species in the layer certainly raises these type of questions.

Once attached on the sand surface the adhesion is evidently strengthened by sintering. Several sintering mechanism can be involved, however, in silicate systems at high temperatures viscous flow is important (German, 1996). Surface diffusion and volume diffusion are also possible. The sintering rate, neck growth

versus particle diameter, X/D_p , is inversely related to the particle diameter in all these mechanisms, being $\sim D_p^{-2}$ for the viscous flow, $\sim D_p^{-4/7}$ for the surface diffusion and $\sim D_p^{-3/5}$ for the volume diffusion. Evidently, the small particle size is favorable for layer densification. Possibly the high Ca concentration decreases the ash viscosity in the layer, thus enhancing the layer densification.

The ash layer did not grow in an unlimited manner. During paper mill sludge and bark co-combustion in the BFB the maximum thickness was about 20 μm , and during pulp mill sludge and bark co-combustion about 100 μm . Apparently the porous ash layer did not resist attrition in the bed once it grew sufficiently thick. During pulp mill sludge and bark co-combustion in the BFB the layer structure was less porous. Evidently, the denser structure increased the maximum layer thickness. During paper mill combustion in the CFB no maximum layer thickness was observed. Indeed, the layer was often as thick as the sand particle itself. On a mass basis about 60 % of the bed material was sludge-derived ash species (Publication 6, Table 5). The layer structure and chemical composition were alike in the BFB and in the CFB. This suggests that the adhesion mechanism is possibly similar in both units, but the rate of attrition is different. As discussed previously the attrition and fragmentation in the CFB should be more pronounced than in the BFB. However, our results suggest that attrition in the bed consumes the formed layer more rapidly in the BFB than in the CFB, and evidently more work is needed to explain the detected difference. The formation of a dense calcium silicate layer on the sand interface during pulp mill sludge and bark co-firing in the BFB cannot be explained here either. Ca-species were not observed to be volatilized, hence, most likely the formation reactions will take place in the solid phase.

4.4 Comparison between BFB and CFB

The test runs with paper mill sludges in the BFB and CFB enabled us to compare the differences in ash formation due to the fluidization mode. The macroscopic combustion characteristics, combustion temperatures, stoichiometry in the furnace and fuel quality, were similar in both units. Wet sludges were flexibly co-fired with wood fuels with high combustion efficiencies. The char mass fraction in fly ash was low in both combustors, typically less than 1-2 %, this was evidently due to the low mass fraction of the formed char and high char reactivity.

The clearest difference in the combustion ashes was that the transformation reactions had proceeded further in the BFB. The crystalline structure analyses showed only initial transformation of the mineral phases in the CFB, while in the BFB the transformation had proceeded further. Most likely this was due to lower combustion temperatures in the CFB especially in the freeboard area.

The particle size was higher in the BFB. This was probably also due to higher temperatures in the BFB, resulting in sintered and less fragmented ash particles. Another possible reason is that the ash fragmentation and attrition in the CFB was more pronounced. Char fragmentation can similarly result in smaller ash particles. The measured fly ash specific surface areas were lower in the BFB, $7 \text{ m}^2/\text{g}$, than in the CFB, $10 \text{ m}^2/\text{g}$, and probably this was due to more sintered ash structure in the BFB. Another indication of the lower ash fragmentation tendency in the BFB was that a separate fly ash type, circulating ash, was formed consisting of large, 100-300 μm , particles. Possibly in the CFB the largest ash particles were more fragmented than in the BFB before they were separated from the bed in the hot cyclone.

Negligible concentrations of ultrafine particles formed via condensation, were measured in the BFB and CFB. This was most likely due to the low fraction of volatilized inorganic species. Neither were the trace elements enriched in the submicron particles. These values were slightly higher in the BFB than in the CFB. Higher freeboard temperature in the BFB was probably the reason for this, but the difference is too small for definitive conclusions.

It can be concluded that the similarities in the ash formation in the BFB and CFB are more pronounced than the differences. Mineral particle sintering was the main ash-forming mechanism in both units and the majority of the ash-forming species were transformed into fly ash. Negligible ultrafine particle formation via condensation took place and the S and Cl species were mostly deposited in the porous bulk ash, resulting in low concentration of gaseous emissions. Another common feature was that the ash did not initiate bed agglomeration in these units.

5. Parametric studies in pilot and bench-scale reactors

5.1 BFB scale-down

The effect of operational conditions on ash behavior is difficult to evaluate on an industrial scale due to several possible interactions with other factors. In this respect the bench-scale studies are important. During this research two approaches were used. Paper mill sludge combustion tests in a pilot-scale BFB were performed with similar bed height, particle size and fluidization velocities as in the industrial units (Publication 2). The cross-section in the pilot BFB was 0.38 x 0.41 m and the test rig has been described in detail by Anthony et al. (1986). The bed dimensions in the bench-scale BFB were much smaller (cylindrical furnace of 0.1 m in diameter) and different operational parameters had to be used to those in the industrial unit (Publication 7). The rig has been described by Nordin (1995 A). Horio et al. (1986) have shown that the bed hydrodynamics can be maintained unchanged when scaling-down the FBC geometry. Their similarity rule states that to achieve an equivalent bubble coalescence the following condition is required:

$$U_0 - U_{mf} = \sqrt{m} (U_0 - U_{mf})^0 \quad (1)$$

where ⁰ denotes the values in the initial conditions, m is the scale factor, U₀ is the superficial gas velocity and U_{mf} is the minimum fluidization velocity. For bubble splitting the following rule applies:

$$U_{mf} = \sqrt{m} U_{mf}^0 \quad (2)$$

The primary interest in our bench-scale tests was to simulate the macroscopic combustion conditions. This was done by adjusting the primary and secondary air feed to achieve similar stoichiometric conditions and temperatures as in the industrial unit. Table 5 presents the main combustion parameters. The ratio of fluidization air and total air is similar to the industrial BFB, resulting in equal combustion staging on both scales. Also the studied temperature was within the

Table 5. The effect of scale down on bed hydrodynamics and combustion properties. Values calculated at 800 °C.

	Case:	A	B	C	D	E	F
Particle size	μm	600	730	430	200		
Static bed height	m	0.6	0.4	0.5	0.04		
Static bed pressure	kPa	5.3	3.5	4.4	0.4		
U_0	m/s	1.5	1.5	1.1	0.20	0.35	0.11
Re_p	μm	7.1	8.7	3.8	0.3		
Scale-down factor, m						10	100
Calculated U_{mf} *		0.17	0.22	0.08	0.03	0.03	0.01
Observed U_{mf} at 800 °C	m/s	0.4	n.a.	n.a.	0.07		
U_0/U_{mf} (calculated)		8.8	6.8	13.8	6.8	13.8	13.8
Fluidization air of total air		96%	55-100%		31%		

Paper mill sludge and bark:

A) Industrial BFB

B) Pilot-BFB

* Mori and Wen (1975)

Pulp mill sludge and bark:

C) Industrial BFB

D) Bench-scale BFB

E) Similarity rule: scale-down from C) by a factor of 1/10

F) Scale-down by a factor of 1/100

same range, and quartz sand was used as the bed material. Hence, the primary goal of maintaining similar macroscopic combustion conditions was achieved. Having set the operating parameters to optimize the combustion conditions, the proper scale-down in the bed hydrodynamic conditions is not obvious. The similarity rule requires a complete geometrical scale-down, which in our case could not be strictly followed. The scale-down factor, m, was, for the bed diameter about 1/100, for the bed height 1/10, for the distributor orifice diameter 1/8 and for the orifice pitch 1/4. The minor scale-down factor in the distributor geometry resulted in a larger initial bubble size than that required by the similarity rule. Correspondingly, the high scale-down in the bed diameter includes the probability of wall interference in the flow field. Matsen (1996) has stated that when the bubble diameter is 10 % of the bed diameter, wall interference is possible, and at 30 % the bubbles are deformed due to the wall

effect. This value was 26 % in the bench-scale unit, calculated with the procedure developed by Mori and Wen (1975), and the wall effect probably affected the bed hydrodynamics. During the scale-down the sand particle size was reduced to 125-250 μm . Both the lower fluidization velocities and smaller particle size resulted in a lower particle Reynolds number. However, in the similarity rule the particle diameter is considered as a microscopic flow field parameter. The calculated U_{mf} corresponded to the scale-down of 1/10. The ratio between U_o and U_{mf} on the bench scale was about half of that used in the industrial unit firing pulp mill sludge and bark and about the same as in the unit firing paper mill sludge and bark.

Results from the bench-scale reactor indicated that the mass fraction of ultrafine ash formed via condensation was not significantly changed due to the scale-down. The ultrafine particle mode less than 0.3 μm included 2.2-5.0 weight-% of fly ash in the industrial unit co-firing pulp mill sludge and bark. When this type of mixture was co-fired in the bench scale, the mode located similarly below 0.3 μm including 4.3 weight-% of the sampled fly ash. The condensed particles were composed of K, Na, S and Cl on both scales and stoichiometric calculations indicated that alkali sulfates and alkali chlorides were the condensed main phases (Publication 7, Figures 3 and 5). Neither was the residual ash formation mechanism changed on the bench scale. The supermicron particles were formed of sintered minerals, and the main fly ash mass mode was within 10-100 μm as in the industrial unit. No molten ash agglomerates in the fly ash were observed. The mass fraction of the fragmented supermicron particles at 0.3-1.0 μm was low, 1.5-1.9 %. Here the similarity to the industrial scale is also evident.

The main difference between the bench-scale and industrial units was observed in the large ash particle accumulation in the bed. As discussed previously, in the industrial BFB the fraction of large ash particles was low, in the order of few percent of the bed mass. Results on a bench scale were different. After three hours of operation, the ash fraction in the bed was over 10 % and growing steadily. The ash was mainly in the form of individual porous particles, but also, a similar layer was formed on the sand surface as in the industrial units. The large particle accumulation in the bed did not take place during a reference test with bark pellets. This suggests that the large particle size during sludge combustion was namely due to the sludge characteristics.

Two reasons for the large particle accumulation in the bench-scale bed can be suggested. Obviously the lower fluidization gas velocity in the bench-scale unit is one reason. According to our results in the industrial BFB, the ash particles have to be over 200 μm until they can remain in the bed (Publication 6, Figure 4). When the particle settling velocities on a bench scale were calculated and compared to the average flue gas velocities in the furnace, the critical size was around 100 μm . A particle density of 2.5 g/cm^3 , particle porosity of 0.5 and shape factor of 2 were assumed. This estimate is consistent with the SEM analyses, where 100 μm ash particles were observed in the bed. However, the accumulated particles were not typically in that range of 100-200 μm , which could be due to the difference in the gas velocities. Sieve analyses showed that the ash particles were larger than the bed sand, over 250 μm . This is also larger than that observed in the industrial units. Therefore, the possibility of lower fragmentation in the shallow bench-scale bed has to be considered. Mullier et al. (1991) have stated that attrition in the distributor area is independent of bed mass, but in the bubbling bed region the bed mass has importance. The bed static pressure is directly proportional to the bed height, being tenfold in the industrial BFB when compared to the bench scale. Presumably, the higher pressure of the deep bed in the industrial unit increased the particle fragmentation.

Similar ash accumulation in the bed was not observed in the pilot BFB firing paper mill sludge. The ash fraction in the bed was stabilized at 3-6 %, which corresponds to the situation in the industrial scale. Neither were extremely large ash particles observed. This suggests that when the fluidization velocity, bed particles size and bed height are the same as in the industrial unit also the ash accumulation mechanisms will remain unchanged.

5.2 Effect of bed temperature

The effect of bed temperature on ultrafine particle formation during pulp mill sludge combustion was studied in the bench-scale BFB. The ultrafine particle mass fraction was assumed to be an indicator of inorganic species volatilization. The results showed that a higher temperature increased the volatilization almost linearly (Publication 7, Figure 4). No threshold temperature, where the volatilization had increased rapidly, was found. Presumably, the peak

temperatures on the char surface were sufficient for volatilization even when the bed temperature was low. Therefore, volatilization was observed already at low bed temperatures and no sudden increase in volatilization took place when the temperature was increased. Another finding was that volatilization was directly connected to the fuel feed. When the fuel feed was stopped but fluidization continued, the ultrafine particle mode disappeared. Evidently, the ash-forming species were volatilized directly during combustion and not due to subsequent reactions in the bed.

The effect of bed temperature on ash particle fusion was studied in 28 fly ash samples from the pilot BFB co-firing paper mill sludge and wood. The bed temperature varied between 710-1,010 °C. Only some of the smallest particles, less than 20 µm, were spherical, indicating that an average ash particle did not melt during combustion. The number of fused particles was low in all samples and no consistent correlation to the bed temperature was found. Obviously sintering remained the principal ash-forming mechanism and melting or fusion was not significant even at high temperatures.

5.3 Effect of sludge moisture and fibrosity

Results in this study suggest that the sludge moisture and fibrosity have a major impact on ash formation. A high moisture content was found to reduce the volatilization of ash-forming species both on an industrial and bench scale. Wet sludge in the fuel mixture rapidly reduced the ultrafine particle concentration to negligible values in the industrial BFB co-firing bark and paper mill sludge (Publication 6, Figures 10 and 11). Experiments with pulp mill sludge in the bench-scale BFB showed that combustion of wet sludge, unlike that of dried sludge, produced low concentrations of ultrafine particles (Publication 7, Figure 4). These results suggest that wet sludge altered the combustion behavior in the fuel mixture. As discussed previously, the sludge moisture has been observed to decrease combustion temperatures in a burning particle and to reduce char formation due to steam vaporization through the pyrolyzing and burning surface layer (Ogada and Werther, 1996). Similarly the pyrolysis phase and the char combustion overlapped significantly due to moisture vaporization. As demonstrated with biomass fuels by Wornat et al. (1995) and Olsson et al. (1997), the volatilization of ash-forming species is related to the char

combustion phase, rather than to the pyrolysis phase. Therefore, in addition to the lower temperatures, it is also probable that the decreased char formation in wet sludge is a reason for the reduced volatilization. It is possible that the overlapping of various combustion phases will reduce the length of the separate char combustion phase, where most of the volatilization takes place.

The sludge fibrosity was observed to change the residual ash particle size. Experiments in the pilot-scale BFB indicated that a more fibrous sludge produced larger ash particles. The sludge labeled as PDS-1 originated from a deinking process and was fibrous, irregular in shape and similar to wet cardboard (Publication 2, Figure 2). Sludge PDS-2 was delivered from another mill using wastes from deinking as well as primary and secondary clarifier (Publication 2, Figure 3). The concentration of ash-forming species was about 30 % (dry basis) in both sludges. Results showed that combustion of the more fibrous PDS-1 produced larger fly ash particles (Publication 2, Figure 8). Presumably, the fibers increased the sludge strength and acted as a connecting structure during the mineral particle sintering. The C_{fix} concentration in the fibrous PDS-1 was slightly higher and it is probable that the higher fraction of formed char aided the formation of sintered particles on the char surface.

6. Ash deposit formation

6.1 Bed agglomeration

Fluidization becomes unstable if the bed material agglomerates. If the ash melts or a liquid layer is formed by condensation or chemical reaction, defluidization is almost inevitable. Experiments with viscous liquids indicate that a thin liquid layer, 0.2-0.4 μm , on the surface of glass particles will reduce the fluidization capability (Willett et al., 1997). Another test run indicated that 0.04 % alkali salt concentrations in the bed defluidized the quartz sand bed at 950 °C (Grubor et al., 1995). However, defluidization may already occur below the ash melting temperature. The bed material will form interparticle bridges at certain temperatures, above which higher fluidization velocities are needed to keep the bed in motion. This is often called the bed sintering temperature (Gluckman et al., 1976, Siegell, 1984). Time has also been observed to be an important factor in defluidization. Mikami et al. (1995) demonstrated with iron spheres that defluidization occurred gradually when the bed temperature was kept constant. This was suggested to be due to sintering via surface and volume diffusion. As a result of their sintering tests with coal ashes, Skrifvars et al. (1994) stated that solid-gas chemical reactions can also form agglomerates when the reaction product creates necks between bed particles.

The ratio between ash and bed material is connected to defluidization. During wood firing in a bench-scale BFB, low concentrations of ash, less than 0.1 % of the bed material, reduced the fluidization properties at 850 °C (Davies and Dawson, 1989). Öhman (1997) indicated that the ash to bed material ratio was the factor that correlated best with the agglomeration temperature in a bench-scale BFB. Also the ash accumulation mechanism among bed particles is significant. As discussed previously, Manzoori and Agarwal (1993) discovered that coal ash was deposited on the surface of the quartz sand and the ash layer agglomerated the bed. The agglomeration growth was a rate process, but consecutive defluidization was an instantaneous phenomenon (Manzoori and Agarwal, 1994). Dawson and Brown (1992) discovered during coal combustion in a laboratory-scale BFB that an amorphous glassy phase was connecting bed particles causing defluidization. In these experiments CaO was observed to react

with quartz sand and it was suggested that this enhanced the bridging between bed material.

Our results suggest that pulp and paper mill sludges are not prone to defluidize the bed at typical combustion temperatures. Bed agglomeration occurred only occasionally in the measured industrial units, e.g. during start-up periods, and was related to technical problems in the fuel feed. Bottom ash sieve analyses were consistently similar to fresh sand indicating that the sand particles did not agglomerate and coarsen the bed (Publication 6, Figure 4). Combustion tests with paper mill sludges in a pilot-BFB did not show bed agglomeration at the studied temperature range up to 1,000 °C (Publication 2, Table 3). The ash concentration was stabilized at 3-6 % in the pilot-BFB as described in the previous chapter. Hence the refractory nature of the ash-forming species and the low concentration of large ash particles among the bed material resulted in non-agglomerating bed behavior.

Another set of bed defluidization tests was carried out in the bench-scale BFB co-firing pulp mill sludge and bark pellets. Three test procedures were used. In the first procedure combustion was stopped after a sufficient accumulation of ash in the bed and the bed temperature was increased by 3 °C/min until defluidization occurred. This method and the test device has been described by Nordin et al. (1995 B). In the second procedure bed fluidization was continued at a stable temperature after the combustion was stopped. With this method the time dependency in defluidization was studied. In the third procedure combustion was carried out at a stable temperature until the bed was defluidized.

The results showed that the mode of ash accumulation in the bed is an essential factor in the bed agglomeration. During the combustion of bark pellets the ash was accumulated in the form of an ash layer covering the sand surfaces (see previous chapter). Here the layer included significant fraction of K. When the ash layer was sufficiently thick a bridge was formed between two bed particles initiating agglomerate growth and bed defluidization (Figure 7). This is similar to the results reported by Manzoori and Agarwal (1993 and 1994) and Compo et al. (1987). In our tests procedure #1 resulted in defluidization at 988 °C (3 °C/min, no combustion). Results with procedure #2 were practically the same (fluidization at a stable temperature). The procedure #3 resulted in

defluidization at 920-930 °C within 30 minutes (combustion at a stable temperature).

During the pulp mill sludge combustion large ash particles accumulated in the bench-scale bed and the ash layer formation was less significant (see previous chapter). Here the bed was agglomerated via sintering of the porous ash particles, and the sand particles participated only occasionally in the agglomerate growth (Figure 8). Defluidization was not an instantaneous, but rather a gradual phenomenon (Figure 9). Using procedure #1, the bed was defluidized within a few minutes at 1,010 °C. With procedure #2 the bed was defluidized gradually at 950 °C, taking more than an hour. With procedure #3 no definitive agglomeration temperature was obtained, because the bed temperatures started to deviate during firing at 950 °C. Temperatures in the upper bed increased whilst the bed bottom remained cool due to reduced mixing in the bed. The temperature deviation was observed beforehand, but the final defluidization occurred within a minute, resulting in a rapid temperature increase in the upper bed. The temperature deviation before defluidization has been also observed by Ergudenler and Ghaly (1993) and Atakul and Ekinci (1989).

The bed agglomerates formed during all the tests with pulp mill sludge were structured by large and porous ash particles. Obviously the defluidization mechanism was the same during all tests, but the test procedure had a significant impact on the results. Lin et al. (1997) distinguished two defluidization mechanisms during bed agglomeration tests with straw on a bench scale. The first mechanism was related to an increased bed particle stickiness due to an ash layer formation on the particle surface, resulting in rapid defluidization. In our tests this type of mechanism was observed with the bark pellets. The other mechanism proceeded via gradual formation of loose jetsam agglomerates, which segregated in the bed bottom and defluidized the bed. Here the similarity with the pulp mill sludge tests is obvious.

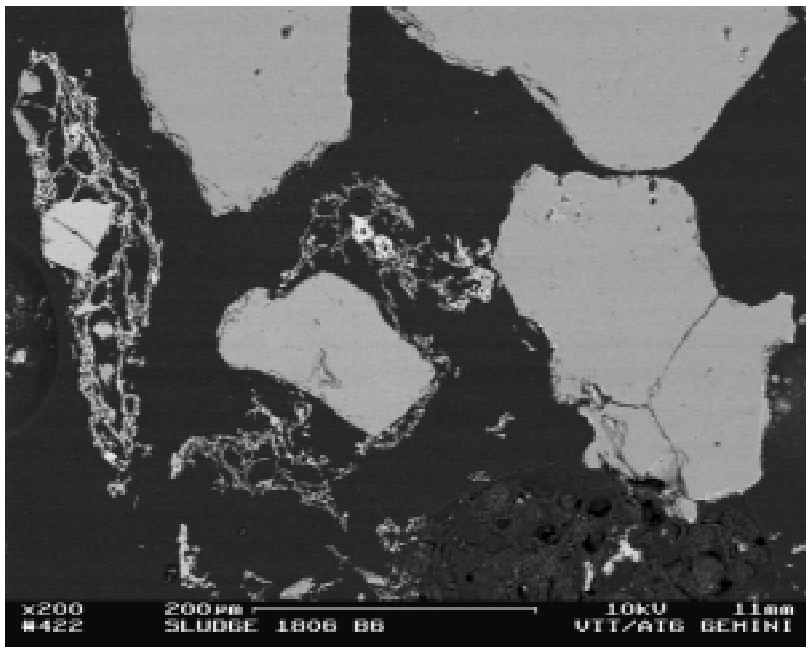
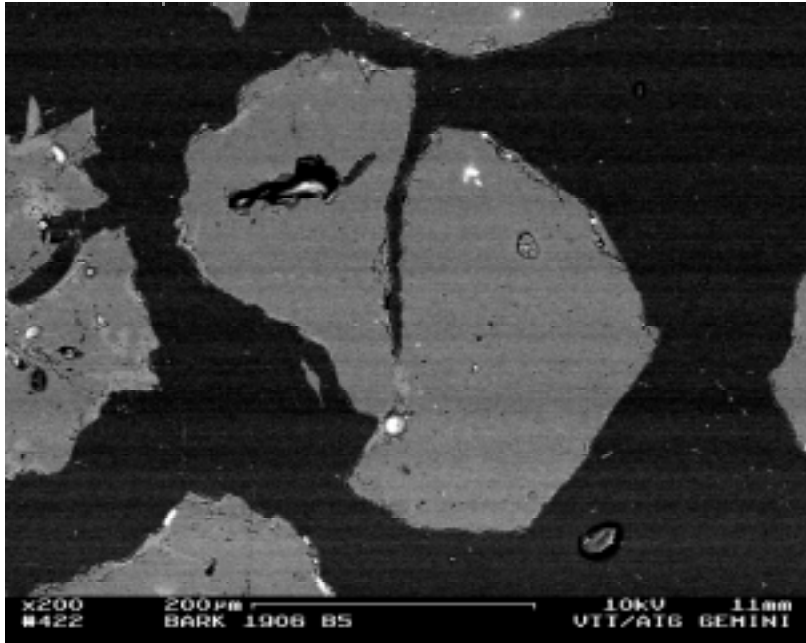


Figure 7. SEM backscattered electron images of agglomerated bed in the bench-scale tests with bark pellets (upper picture) and pulp mill sludge (lower). Dense gray particles are quartz sand, porous agglomerates are ash and dark background is epoxy.

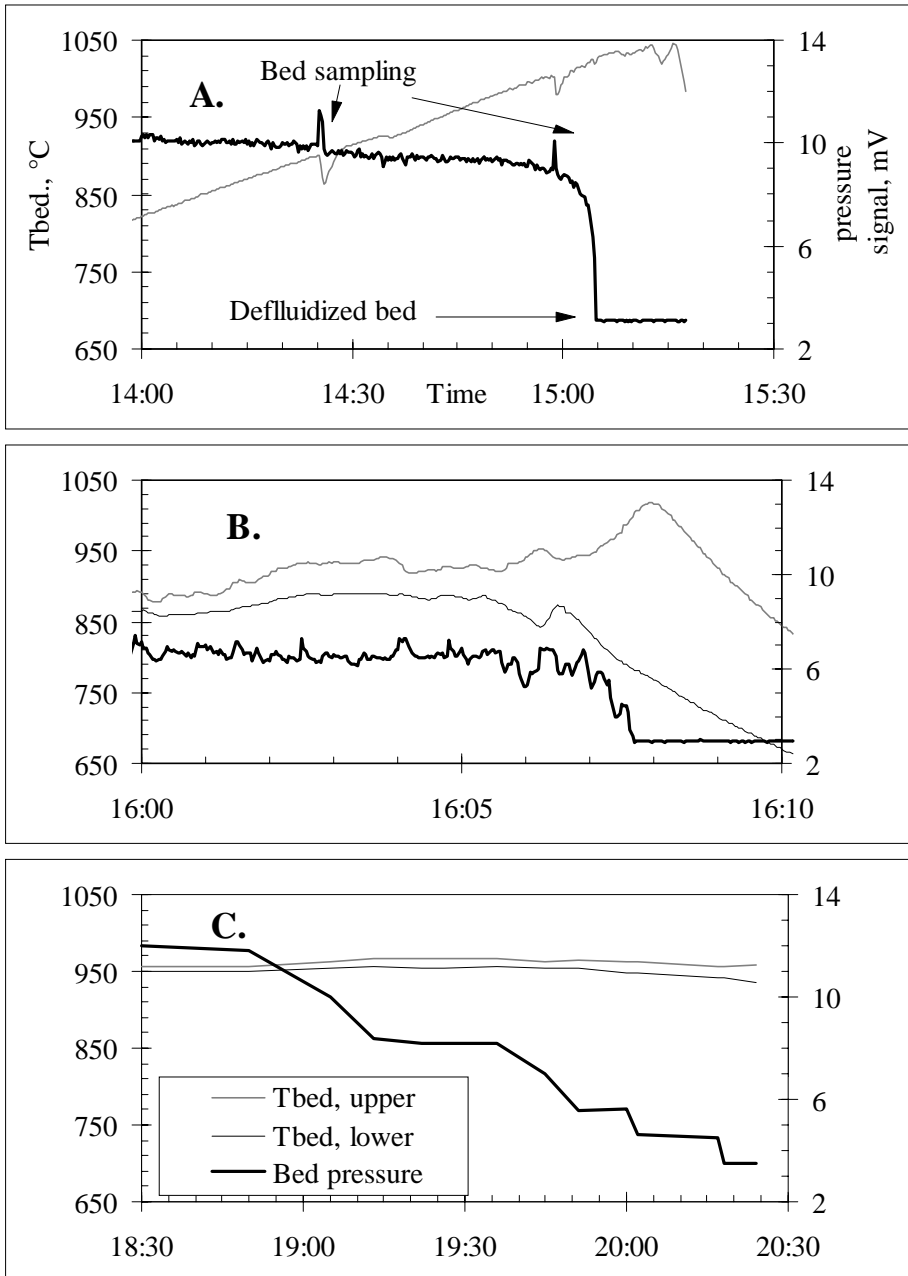


Figure 8. Bed temperature and bed pressure signal during bed agglomeration tests with pulp mill sludge. A. Procedure #1, B. procedure #2 and C. procedure #3.

The difference in defluidization mechanisms is also visible in the bed sieve analyses. Figure 9 illustrates the weight fraction of bed particles over the size of fresh sand particles, 250 μm , during the test runs. When bark pellets were fired, the fraction of agglomerates was low until the sand coating was sufficient, and the bed coarsening increased rapidly due to the agglomeration of the coated particles. The agglomerates typically contained few sand particles, and no large agglomerates were observed at this point. Bed agglomeration resulted in a sudden defluidization. During pulp mill sludge combustion the bed was coarsened by the ash particle accumulation in the bed and not sand particle agglomeration. Hence the coarsening was related to the sludge feed rate and the fraction of large particles grew linearly. This resulted in gradual defluidization and no rapid increase in the coarse particle fraction took place. During co-combustion of bark and sludge, similarities with both defluidization mechanisms were observed. The bed coarsening was not linear, but the final defluidization occurred gradually, as it did during the sludge combustion.

Earlier findings showed that the ash formation and accumulation mechanisms have a significant impact on the bench-scale test results. Evidently, the ash accumulation in the bed should be similar in the test conditions as on an industrial scale. This was not achieved with the pulp mill sludge, so the test results are only indicative for industrial users. With bark pellets the correspondence with industrial beds was better. Nevertheless, the tests showed that the defluidization temperature is higher for the pulp mill sludge than for bark pellets. This was presumably due to the higher K content in the ash layer during bark combustion, which resulted in lower viscosity on the sand surface. Another finding was that defluidization occurred at much lower temperatures during combustion than without it. Evidently, combustion creates locally high temperatures in the bed suspension, which probably triggered the bed agglomeration. As the bed becomes coarser the heat exchange in the bed is decreased, resulting in higher temperature differences and defluidization. Probably, other combustion-related mechanisms will also enhance the bed agglomeration, e.g. direct adhesion of ash from burning char to the sand surface.

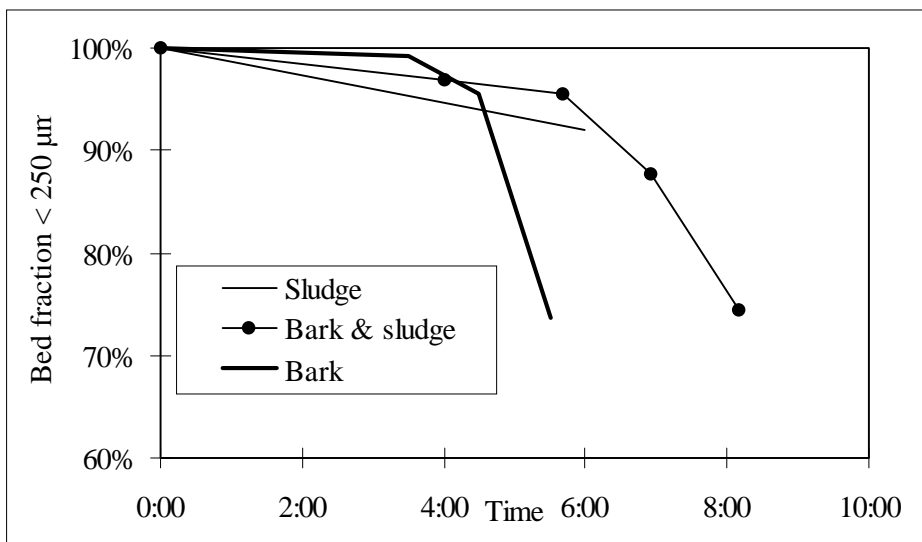


Figure 9. Bed coarsening during combustion and agglomeration tests in the bench-scale BFB. The end point of each curve presents the situation in the defluidized bed.

6.2 Furnace wall deposits

Although not as much studied as bed agglomeration, furnace deposit growth is a common problem in industrial units, e.g. it was observed in the all BFB units in this work. Large clumps can fall from the deposit into the bed resulting in bed coarsening and defluidization. It was observed during paper mill sludge and bark co-combustion in the BFB, that sintered ash acted as binding media between sand and large ash particles (Publication 4, Figures 7 and 8). Ash chemical composition in the deposit was similar to the bulk ash and no condensation of volatilized species on the deposit was observed. Neither was any ash melting detected. These results suggest that formation of a liquid layer, chemical reactions or particle stickiness were not the adhesion mechanisms.

A probable explanation of the deposit growth is ash particle gravitational settling and successive sintering. The deposited particles were typically larger than the fly ash mass median size, including also sand particles (Publication 4, Figure 7). These particles are too large to be transported on surfaces by diffusion or thermophoresis. However, particles do not flow uniformly upward

in the furnace. The flue gas velocities are low in the vicinity of the furnace wall where particles fall downwards, as observed e.g. by Horio et. al (1980, 1983). They detected a strong particle downflow within the nearest 20 mm on the furnace wall. Quite likely, the largest particles are favored by this transport mechanism due to their higher settling velocity. The falling particles settle on horizontal or rough surfaces. Sintering will densify the structure and create bonding between ash and sand particles.

When paper mill sludge and bark was co-fired in the BFB, the deposit was thin, about 50 mm, and friable. When pulp mill sludge and bark was co-fired in the BFB, the deposit grew thick, about 500 mm, and dense, and had to be removed during a boiler outage. Presumably, the limited deposit growth with the paper mill sludge was due to the higher ash viscosity. The paper mill sludge bulk ash viscosities at 900 °C calculated with the function developed for silicate systems by Urbaine et al. (1981) were about 700 Pa s (Table 6). This value was 130 Pa s in the BFB co-firing pulp mill sludge and bark. The calculated viscosities in the deposit ash structure as measured by WDS were within the same range, however, local differences due to heterogeneous particle structure existed. The wall deposits were also observed in the bench-scale BFB firing pulp mill sludge. Bed temperatures up to 950 °C were used. The sand weight fraction in the deposit was constantly 20-40 % regardless of the fuel or unit size.

Wall deposit was not formed in the pilot-BFB firing paper mill sludge. Instead, a 1-5 mm thick and very friable ash layer covered the refractory lining at the secondary air zone after several weeks of test run. Sand particles were not attached in the structure. The deposit included only micron size particles and the deposit chemical composition was similar to bulk ash. Ash melting or condensation was not observed. Apparently the particle adhesion, by surface forces rather than gravitational settling, acted as the deposition mechanism. Therefore the smallest particles, having higher adhesion forces per weight, were deposited. Sintering densified the deposit structure after adhesion. Calculated ash viscosities at the measured freeboard temperatures of 1,000-1,150 °C were 815-10,500 Pa s. Apparently this was too high to allow attachment of the larger particles via particle settling and consecutive sintering.

Table 6. Ash viscosities at 900 °C as calculated with function developed for silicate systems by Urbaine et al. (1981). Ash composition in the deposited ash was measured with WDS.

Unit	Fuel	Viscosity of bulk ash (Pa s)	Visc. of deposited ash (Pa s)	Ash weight fraction in the deposit
Pilot BFB	Paper mill sludge	57,990	83,500	100 %
Industrial BFB	Paper mill sludge and bark	694	256-1631	70-75 %
Bench-scale BFB	Pulp mill sludge	2588	1214-2771	60-80 %
Industrial BFB	Pulp mill sludge and bark	130	43-225	60-80 %

It can be concluded that the ash particles are able to initiate deposit growth on the furnace wall if the ash viscosity is sufficiently low at the freeboard temperatures. When paper mill sludge was co-fired with bark, smaller deposits were formed than with pulp mill sludge and bark. When only paper mill sludge was fired in the pilot-BFB, the deposit growth was negligible. Estimates in this study indicate that if the ash viscosity is less than 1,000-3,000 Pa s, the fireside deposits are formed. Above that limit only the smallest particles are attached, presumably by surface forces. According to Raask (1985) viscosities in non-flowing slag during coal combustion are 10^3 - 10^5 Pa s. This is within the range calculated for the deposits. Senior and Srinivasachar (1995) showed that in pulverized coal combustion the critical viscosity for particle stickiness on heat exchangers via inertial impaction is 10^5 - 10^8 Pa s. This is definitely higher than that measured in the deposits studied here. Obviously the ash densification by sintering rather than the adhesion of sticky particles is the crucial factor for the deposit growth presented above.

7. Elemental enrichment

7.1 Main elements

When firing paper mill sludge no significant elemental enrichment in submicron ash was observed. Apparently the ash-forming species remained in the solid phase, hence enrichment by condensation or gas-phase reactions remained negligible. Ash species were found in similar concentrations in the fly ash and in the ashed fuel (Publication 4, Figure 12 and Publication 6, Tables 4 and 5). During pulp mill sludge firing K, Na, S and Cl species were volatilized and enriched in the submicron ash (Publication 7, Tables 2 and 3). These species were also deposited in the supermicron particles, hence they were not significantly depleted in the residual ash. The non-volatile species were mainly in the supermicron particles.

Elemental enrichment in the bottom ash is studied in Table 7 by dividing the elemental mass fractions in the bottom ash by the elemental mass fractions in the bulk ash. This can be compared to the mass fraction of fuel-derived species in the bottom ash. Hence, a higher value in the elemental concentration than in the total ash concentration in the bed indicates elemental enrichment in the bottom ash. These results did not show consistent enrichment of the non-volatile elements in the bed material. When co-firing paper mill sludge and wood waste in the CFB, some enrichment was detected for Ca and Mn. Similarly during pulp mill sludge and bark co-combustion in the BFB, Ca was enriched in the bottom ash. Possibly this was due to reactions between Ca-species and sand (Publication 7, Figure 8). The alkali species, K and Na, were slightly enriched in the bed material in the industrial BFB units. The total concentrations are low, typically less than 5 % of the bed weight, and partly due to mineral impurities included in the sand or wood. Alkali enrichment in the bed was not observed in the bench-scale BFB where pure quartz sand was used. However, the test periods, 8 h or less, were too short for a definitive conclusion. The enrichment of K in quartz sand has been observed during willow combustion in a CFB by Skrifvars et al. (1997). This was suggested to be due to formation of potassium silicates.

Table 7. Elemental concentrations in bottom ash divided by concentrations in bulk ash. Division according to volatility is based on tests with pulp mill sludge (Publication 7, Table 2).

	Paper mill sludge & wood fuels		Pulp mill sludge & bark	Wet pulp mill sludge	Dried pulp mill sludge
Industrial: Ash in bed	CFB	BFB	BFB	Bench-scale	BFB
	0.5-0.6	0.10-0.15	0.10-0.15	0.10-0.15	0.3
Non-volatile main elements					
Si	1.54	2.35	3.19	2.38	2.07
Al	0.70	0.15	0.2 *	0.16	0.32
Ca	1.01	0.13	0.34 *	0.12	0.31
Mg	0.61	0.09	0.19 *	0.12	0.28
Mn	0.93	0.26	0.28	0.12	0.32
Fe **	0.77	0.43	0.70	0.18	0.99
P	0.28	0.14	0.27	0.13	0.31
Ti	0.63	0.15	0.6 *	0.54	0.65
Volatile main elements					
K	0.44	0.60	0.58 *	0.19	0.31
Na	0.88	0.57	0.05 *	0.14	0.29
S	0.68	0.01	0.01	0.03	0.03
Cl	0.13	0.09	0.01	0.01	0.01
Non-volatile trace elements					
Sr	0.80	0.27	0.54	0.13	0.31
V	0.88	0.31	0.68	0.13	0.44
Volatile trace elements					
As ☒	1.22	3.90	0.29	0.33	2.00
Pb	0.13	0.15	0.21	0.20	0.19
Rb	n.a.	n.a.	0.44	0.23	0.26
Semi-volatile trace elements					
Ba	0.39	0.28	0.75	0.13	0.29
Cu	0.83	0.72	0.17	0.19	0.58
Zn	1.09	0.23	0.20	0.10	0.28

n.a. = not analyzed

** possible contamination from steel

* sand-derived fraction reduced from results ☒ close to detection limit

S and Cl were depleted from the bottom ash (Publication 4, Table 3). The only exception was the paper mill sludge combustion in the CFB, when S was in a similar concentration in the bed sample as in the bulk ash. Condensation of Cl species will not take place at the typical furnace temperatures of 800-1,000 °C, hence depletion of Cl in the furnace samples is understandable. However, many S species do condense or react with solid compounds at these temperatures. There does not seem to be any definitive explanation for the observed sulfur depletion. It is possible that kinetic restrictions limit the condensation or reactions of S species. However, sulfation of e.g. CaO in fluidized bed combustors during coal combustion is able to capture 70-90 % of the fuel sulfur. Hence, the suggestion of kinetic restrictions is questionable. The mass fraction of Ca species in the bed is high and Ca species were observed to react with sulfur in the fly ash. However, in the bottom ash negligible concentrations of water-soluble Ca^{2+} were detected, indicating very low sulfation rates (Publication 7). Another explanation is that the Ca, K and Na species remaining in the furnace form silicates with other ash species and are not reactive with sulfur, or they release the sulfur they include. This suggestion is supported by the fact that the FBC furnace ashes included Ca and K silicates, while no sulfates were observed in the crystalline phase analyses (Publication 6, Table 6). The inactivity of calcium silicate in sulfur capture has been discussed e.g. by Anthony et al. (1997).

7.2 Trace elements

Trace elements in the paper mill sludges originate mainly from the recycled paper and clay additives. Hamm and Gottsching (1988) found in their breakdown of Cd, Cu, Cr, Pb and Ni in paper mill mass flows that Cd, Cu and Ni were derived from the recycled paper, while Cr and Pb originated mostly from clay. In the mill outlet most of these elements were found in the produced paper. The main exceptions were Cu, being in the deinking sludge (68 %), and Cd, which was mostly in paper but also in the mill sludge (23 %) and in the mill effluent (24 %). Trace element concentrations were more pronounced in the pulp mill sludge than in the paper mill sludges (Publication 6, Tables 4 and 5 and Publication 7, Table 2). Ashed pulp mill sludge contained higher

concentrations of Cd, 19 µg/g Ba, 2830 µg/g, Mn, 32 000 µg/g and Zn, 1810 µg/g, while the concentration of Pb, 62-225 µg/g, was higher in the ashed paper mill sludges.

Coal-derived trace elements have been divided into the following groups by the International Energy Agency, IEA (1987): i) Volatile elements that remain in the gas phase at flue gas outlet temperatures of 100-150 °C. Some Hg species belong to this group. Fortunately, the concentration of Hg in the pulp and paper mill sludges is very low and typically less than the detection limit (Raitio, 1992). ii) Volatile elements that are transformed into the gas phase during combustion, but condense back to the solid phase. Concern with these elements is their enrichment in fine particles by condensation. Elements belonging to this group in the pulp and paper mill sludges are: As, Cu, Mo, Pb, Sb and Zn. Cd, Sb and Se are also volatile, however, Cd originates mostly from wood fuels, and concentrations of Sb and Se are close to the detection limit. iii) Non-volatile trace elements that are found in the supermicron particles and are depleted in fine ash. In pulp and paper mill sludges this includes Ba, Co, Mn, Rb and Sr. iv) Trace elements indicating intermediate behavior; Cr, Ni and V belong in this category.

The survey by Linak and Wendt (1993) divides trace elements according to their toxicity. Elements with the highest toxicity are As, Cr, Pb and Ni. Be, Cd and Hg also belong to this group, however, their concentration in sludge is very low or below the detection limit. Sludge-derived elements with potential toxicity are Co, Cu, Fe, Mn, Mo and Zn. Of minor toxicity are Sb, Ba, Mg, Sn, Ti and V. Hence, As, Cd, Cr, Cu, Mo, Ni, Pb, and Zn are the elements of highest concern in the pulp and paper mill sludges due their possible enrichment in fine particles combined with toxicity. Division between the volatile and non-volatile elements is not definitive, but dependent on the fuel and the combustion technique. Linak and Wendt indicated in their summary that Ba, Rb and V belonged more often to the volatile element group ii) rather than the groups iii) or iv) as reported by the IEA (1987).

Table 8 compiles the trace element enrichment measurements carried out during this study. The gas-phase concentrations in the boiler outlet were not measured, but presumably they were low due to the negligible concentrations of the highly volatile Hg in the sludge. With both sludge types As belonged to group ii) of the

Table 8. Trace element enrichment in various test runs with pulp and paper mill sludges.

Enriched, (depleted)	Submicron fly ash particles	Bulk fly ash	Fuel-derived bottom ash
Paper mill sludge and wood fuels:			
Industrial BFB (Publication 6, Table 4 and Table 7)	As, Bi, Cd, (Co), (Cu), (Ni), (Rb), (V), (Zn)	(As)	As, B, Co, Cu, V
Industrial CFB (Publication 6, Table 5 and Table 7)	As, (Cd), (Cu), (Ni), (Pb), (Rb), (V), (Zn)	(As)	As, Co, Cu, Mn, Sr, V, Zn, (Cd), (Pb)
Paper mill sludge:			
Suspension combustor (Publication 3, Table 3)	Hg, Cu, Mo, Pb, Zn, (Ba), (Co), (Mn), (Ni), (Sr), (V),	Ba, Sr, (Cu), (Hg), (Mn), (Pb),	Cu, Mn, Ni, Pb, Sr, (Hg)
Pulp mill sludge and bark:			
Industrial BFB (Publication 7, Table 2)	As, Ba, Cd, Cu, Pb, Rb, Zn, (Co), (Sr), (V)	Co	Ba, Sr, Zn
Bench-scale BFB			
Wet pulp mill sludge combustion (Publication 7, Table 3 and unpublished data)	As, Cd, Pb, Rb, (Ba), (Cu), (Co), (Cr), (Ni), (Sr), (V), (Zn)		As, Ti
Dried pulp mill sludge combustion (Publication 7, Table 3 and unpublished data)	As, Cd, Cu, Mo, Pb, Sn, Zn (Ba), (Co), (Ni), (Sr), (V),		As, Cu, Ti, V

volatilized/condensed species, and during pulp mill sludge combustion so too did Cd, Pb and Rb. During pulp mill sludge and bark co-combustion in the industrial BFB, Ba and Zn indicated similar behavior, however, these elements mostly originated from bark. Some of these elements indicated enrichment also in the bottom ash. This may have proceeded via condensation or chemical reaction. Although condensed phases were not detected in the bottom ash, e.g. the concentrations of S and Cl were negligible, this explanation cannot be excluded. Neither could we define if chemical reaction was responsible for the enrichment. Experiments in a bench-scale BFB with lead nitrate and lead chloride by Ho et al. (1994) indicated that the chemical reaction between volatilized lead species and limestone, and in a minor degree with sand, can act as a capture mechanisms.

The non-volatile behavior of group iii) was observed for the following toxic elements: Cr, Ni, Co, and Mn. These elements were detected in submicron ash in low or negligible quantities. During paper mill sludge combustion Cu and Zn were also non-volatile. These elements indicated volatility during combustion of dried pulp mill sludge in the bench-scale BFB, but not when wet sludge was fired (Publication 7, Table 3). During pulp mill sludge and bark co-combustion in the industrial BFB their volatility and enrichment in fine particles was obvious, however, they originated mostly from the bark. Non-volatile trace elements with lower toxicity were Ba, Sr and V. Ba indicated volatility during co-combustion of pulp mill sludge and bark in the industrial BFB, but not when firing pulp mill sludge on a bench scale. This confirms that the volatilized Ba originated from bark. Enrichment in the bed material was occasionally detected for Co, Mn, Sr and V. However, there is no clear indication that the non-volatile behavior is connected to enrichment in the bed material.

Several elements indicated intermediate behavior (group iv). Pb and Rb were volatile during pulp mill sludge combustion, but not when paper mill sludge was fired. Possibly they were associated with volatile species in the pulp mill sludge, e.g. with Cl and S. It has been shown by Jakob et al. (1996) that a high chlorine content will enhance trace metal volatilization. Also the fluidization mode indicated some importance. Paper mill sludge and wood co-combustion in the CFB did not volatilize Cd, but in the BFB a slight enrichment in the submicron ash was observed. Possibly the higher combustion temperatures in the BFB freeboard increased volatilization. Results from the gas suspension combustor offer a basis for the evaluation of trace element behavior at high temperatures (Publication 3, Table 3). The volatile, Pb, and semivolatile elements, Cu, Mo and Zn, in the fluidized bed combustors were clearly volatilized. However, even in these extreme conditions the following trace elements were not volatilized: Ba, Co, Mn, Ni, Sr and V. As discussed above, some of these elements, e.g. Ba, Ni and V, have indicated volatility during coal combustion. Presumably, the clay based minerals in the paper mill sludge efficiently absorb the trace elements, hence reducing their volatility even at high temperatures. Kaolinite is known to efficiently capture volatile alkali vapors via a combination of chemical and physical processes (Uberoi et al., 1990). Results for Pb and Cd are similar (Uberoi and Shadman, 1990). The capture of Cd in kaolinite was less pronounced and the diffusion of volatile species in clay particles was found to be a limiting factor (Uberoi and Shadman, 1991). Evidently, the small clay particle size in sludges enhance the trace element capture. The capture of volatile species by bed sand is also possible as discussed previously. This has also been observed by Ho et al. (1992), who detected an efficient capture of Pb by sand during combustion tests in a laboratory BFB.

In addition to their low tendency to volatilize, trace elements did not show a significant diffusion in the solid-phase. Microscopic analyses of fly ash particle cross-sections sampled during paper mill sludge combustion in the BFB showed that elemental diffusion is related to ash fusion (Publication 5, Figure 1). The elements were unevenly dispersed in a non-fused structure, while in the fused particles the concentration profiles were fairly uniform.

8. Conclusions and recommendations

Ash formation during fluidized bed combustion of pulp and paper mill sludges has been experimentally studied. The thesis concentrated on defining the effect of two different sludge types, paper mill sludge and pulp mill sludge, on ash formation. Measurements with paper mill sludges and wood fuels were carried out in an industrial BFB and CFB and in a pilot BFB. Correspondingly the ash formation in a different fluidization process, BFB and CFB, was studied. Pulp mill sludge was co-fired with bark in an industrial BFB and in a bench-scale BFB. The effect of scale-down on the ash formation was described. Thermogravimetry, BET-surface area measurements, chemical bulk analyses, crystalline phase analyses, particle size measurements and high-resolution microscopy were used for the characterization of sludge and the residual ash. The volatilization of ash-forming species was studied by measuring the concentration of submicron particles formed via condensation using aerosol measurement devices. The enrichment of volatile species and trace elements in the submicron ash was determined by chemical analyses. Ash enrichment in the bed, bed agglomeration and defluidization were studied in a pilot BFB and in a bench-scale BFB. Furnace wall deposits were characterized with chemical analyses and microscopy.

Refractory clay minerals, kaolinite and talc, and calcite were the main ash-forming species in the paper mill sludges. The concentration of volatile species was low, S 0.1 weight-% and Cl less than 0.1 %. The concentration of Na species in the ashed samples was 0.2-0.6 % and K species 0.2-0.9 %. Si, Al, Mg and Ca were also the main ash-forming elements in the pulp mill sludge, but the concentration of volatile species was higher, S 1.1 % and Cl 0.6 %, . The concentration of Na and K in the ashed sludge was 3.0 weight-% and 1.3 %. Ashed pulp mill sludge included higher concentrations of Cd, Ba, Mn and Zn, while Pb was more abundant in the ashed paper mill sludges.

According to the mass flows in the industrial processes more than 90 weight-% of the ash-forming species in both sludge types was transformed into fly ash. The rest of the ash-forming species remained in the bottom ash. More than 93 weight-% of the fly ash was in the supermicron range and the mass median size was 7.5-15 μm . This was much larger than the clay mineral size in the sludge originating from paper making, 0.5-3 μm . The ash particles were formed of

sintered mineral particles and their morphology was similar to the micron-size mineral particle clumps on the fiber surface. Obviously the small mineral particle size and intimate contact with other mineral particles on the sludge fibers enhanced sintering. Combustion tests of paper mill sludges in a pilot BFB indicated that a fibrous sludge produced large ash particles. Especially the concentration of deinking sludge increased the particle size.

Molten ash particles were rarely detected in the fly ash samples, suggesting that the temperatures in the burning sludge did not exceed the ash fluid temperature. The ash-forming minerals in the paper mill sludge partly lost their crystalline structure in the fly ash and formed amorphous phases, calcium silicate and alkali silicate. These reactions were more pronounced in the ash particles that remained for a longer period in the furnace than in the average fly ash. This finding suggests that after the residual ash particles are formed, slow reactions between the ash-forming minerals take place, possibly in the solid phase. The suggestion of solid-phase reactions is supported by the thermogravimetric analyses, which did not show phase transitions at the studied temperatures less than 1,200 °C. Another finding was that the reaction rates were lower in the CFB than in the BFB; probably higher combustion temperatures in the BFB freeboard enhanced the reactions. The formed residual agglomerates were porous and friable. Paper mill sludge fired in a gas suspension resulted in a larger fly ash particle mass mean size, 300 µm, than in the CFB, 7.5 µm, or in the BFB, 12 µm. Evidently, fragmentation and attrition in the bed reduced the particle size in the FBC units. The smaller particle size in the CFB was presumably due to more pronounced attrition in that unit.

Co-combustion of pulp and paper mill sludges with wood fuels produced spherical particles via condensation and their agglomerates due to collisions of particles smaller than 0.3 µm. Combustion of paper mill sludge resulted in negligible ultrafine particle mass concentrations. On a number basis this mode was detected at 0.05 µm in the BFB, but in the CFB no clear mode was observed. Assuming that the volatile species were not entirely absorbed in the formed ash, the low ultrafine particle concentrations were due to negligible inorganic species volatilization. However, the assumption of volatile species deposition in the bulk ash has to be considered. The ash-forming minerals in the paper mill sludge, namely kaolinite and calcite, are known to react with K, Na, S and Cl species. Laboratory experiments in this study indicated that the residual

ash in the paper mill sludge is able to capture part of S and Cl even at 1,350 °C. Possibly the small mineral particle size in the sludge and the porous structure of the residual ash enhanced the absorption.

When co-firing pulp mill sludge with bark in the industrial BFB, the ultrafine particle (less than 0.3 μm) fraction of the fly ash was also significant on a mass basis, 2.2-5.0 %. The condensed species included K, Na, S and Cl. Evidently, the higher concentration of these species in the pulp mill sludge than in the paper mill sludges resulted in their more pronounced volatilization. The sludge moisture decreased the formation of ultrafine particles in the bench-scale tests, presumably due to reduced inorganic species volatilization. This was probably because of lower combustion temperatures on the char surface, and reduced char formation due to moisture evaporation. Also, overlapping of the char combustion phase with fuel drying and pyrolysis may reduce volatilization.

The volatile species were condensed only partially on the ultrafine particles. The volatile main elements, K, Na, S and Cl were concentrated in the ultrafine particle mode by 9.2-35.1 % in the BFB co-firing pulp mill sludge and bark. During paper mill sludge firing these fractions were negligible. The mass concentrations were much higher for the supermicron particles than for the ultrafine particles and the measured surface area concentrations in the bulk ashes were high, 7-10 m^2/g . Evidently therefore, heterogeneous condensation and chemical reactions transported most of the volatilized species in the supermicron particles.

Ash species were concentrated in the bed via two pathways. The largest ash particles, over 200-300 μm , were not entrained from the bed by flue gases. Chemical composition in these particles was similar to bulk ash and they did not initiate bed agglomeration in the industrial units. Another ash type in the bed was formed of micron-size particles attached on the sand surface presumably by surface forces. These particles formed a porous and sintered layer. No condensed species were observed. The layer included mainly non-volatile species especially Ca. The ash layer did not cause bed agglomeration at the studied temperatures up to 1,000 °C. During bark pellet combustion in the bench-scale BFB a similar layer was formed including higher concentrations of K. Fluidization at 988 °C resulted in agglomerate growth and rapid

defluidization. Presumably, K species decreased the ash layer viscosity and caused the bed agglomeration.

The BFB scale-down when co-firing pulp mill sludge and bark did not have any marked effect on the ultrafine particle formation via condensation of the volatilized inorganic species. The mass fractions of the ultrafine particles in the fly ash and the particle morphology were similar on both scales. Also the particle compositions were alike including K, Na, S and Cl species. This suggests that the same inorganic species were volatilized during combustion, and probably the volatilized quantities were similar. However, the ash behavior in the bed was changed due to the scale-down. The fluidization velocities on a bench scale were much lower than in the industrial unit resulting in a steady accumulation of large ash particles in the bed. The size of the accumulated particles was larger on a bench scale than that observed in the industrial unit. Presumably, this was due to reduced fragmentation in the shallow bench-scale bed. Ash accumulation in the bed resulted in the formation of large sintered agglomerates that gradually defluidized the bed at 950 °C.

Wall deposits including large ash particles and sand were formed on the BFB furnace wall. Most likely these particles were transported on the deposit from a down-flowing particle flux near the furnace wall. Once deposited the ash sintered and formed a binding structure between the sand particles. Composition of the deposited particles was similar to bulk ash analyses. No molten ash or condensed ash species, namely S and Cl, were detected in the deposit. Hence the long residence time in the high-temperature zone was the reason for ash sintering. The deposit formation was more pronounced when co-firing pulp mill sludge. Estimative calculations indicate that the viscosity in the pulp mill sludge ash was lower than in the paper mill sludges and evidently this resulted in denser ash structure. The calculations suggest that when the ash viscosity is less than 1,000-3,000 Pa s this type of deposit can be formed.

During paper mill sludge and wood fuel co-combustion in the fluidized beds, only moderate trace element enrichment in the submicron ash was detected. During pulp mill sludge and bark co-firing the toxic As, Cd, Pb and less toxic Rb were enriched in the submicron particles evidently via volatilization and successive condensation. In both sludge types the non-volatile elements with evident or possible toxicity were Cr, Ni, Co, and Mn. Other non-volatile trace

elements were Ba, Sr and V. Cu and Zn species showed intermediate behavior. They were non-volatile during the combustion of wet pulp mill sludge, but when the sludge was dried they indicated volatility. During paper mill sludge firing at high temperatures in a gas suspension, up to 1,300 °C, Cu and Zn species were volatilized.

This study shows for industrial users that pulp and paper mill sludges can be fired in fluidized beds without bed agglomeration at typical combustor temperatures of 800-900 °C. Part of the ash remained in the bed, but this was not connected to agglomeration problems or trace element enrichment. Ash deposits were formed on the furnace wall in the industrial BFB units due to sintering of large ash particles and incorporation of sand in the structure. These results suggest that the paper mill sludge ash is not prone to create large deposits, unlike the pulp mill sludge, which in the studied unit required furnace wall cleaning.

Another important finding was that the fly ash is mostly in the supermicron size range. This is beneficial for conventional flue gas cleaning devices that are most effective in this particle size. This is especially true for paper mill sludges, producing negligible concentrations of submicron ash particles via condensation and very low trace element enrichment in the fine ash. The concentration of the condensed submicron particles was more significant when firing pulp mill sludge. Also the trace element enrichment in the submicron ash was more pronounced. The elements of highest concern are As, Cd and Pb, however, none of them showed alarming concentrations in the submicron ash. The capture efficiency of S in the fly ashes was high and correspondingly the gaseous SO₂ emissions were low. Comparison between bubbling and circulating fluidization did not indicate significant differences in the ash-forming mechanisms. The fly ash particle size was smaller in the CFB, probably due to higher fragmentation and attrition in this unit.

This research was limited to the ash behavior in the furnace. The natural continuation would be to study the ash problems downstream of the furnace. Mill visits during this study indicated that pulp mill sludges especially are prone to increase superheater fouling and corrosion. This suggests that the measured higher mass fractions of volatilized inorganic species during the pulp mill sludge combustion are probably connected to the ash problems downstream of the furnace. Another important issue is the ash leachability, which is most likely affected by the concentrations of S and Cl. This study raised several questions and many of them remained unanswered. S was depleted in the furnace ashes although Ca and alkali species were available. Probably more experimental work is required where the role of silicate formation is related to S depletion in combustion ashes. Of further interest are the ash species reactions in the bed, where diffusion of Ca into the quartz sand was observed. More research is also needed to define which ash characteristics are important in the bed agglomeration. As these separate problem areas are being distinguished a more detailed and fundamental approach is required. Therefore bench-scale studies and modeling are needed. Hopefully results in this study give useful information on the inorganic species volatilization and ash particle formation for future studies.

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