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Fly ash particle formation in kraft recovery boilers

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VTT Chemical Technology

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Abstract

Fly ash particle formation in the recovery boilers has been studied experimentally in five industrial scale recovery boilers operating in Finland. The formation and growth mechanisms of the particles were studied by measuring particle characteristics including number, mass and composition size distributions in the gas phase at the recovery furnace exit, at superheater area and at boiler exit. As part of the thesis work, measurement methods were developed for recovery boiler conditions. Electron microscopy was utilised to study the particle morphology and in the case of the coarse particle study, to determine the compositions of various particle types. During this study, a method for the direct determination of chemical compounds in the particles was applied along with the traditional chemical analyses methods. In addition to the experimental studies, the particle formation was simulated with an Aerosol Behaviour in Combustion (ABC) model, which includes models for gas-to-particle conversion and for deposition.

The particle size distribution was found to be trimodal at the furnace and bimodal at the boiler exit. Unlike in other boilers burning solid or sludge fuels, most of the particle mass appeared in the particle size fraction smaller than 5 µm, i.e. in fume particles. The average size of the fume particles remained constant at almost 2 µm in aerodynamic mass mean diameter in the convective sections of all five boilers. However, the mass concentration increased while the boiler heat load increased. The coarse particle concentration was dependent on the boiler operation and on sootblowing. Carryover particles were detected only in the furnace.

The results indicate that seed particle formation is involved in the fume particle formation. In the measured case, the seed forming elements Fe and Mn, showed clearly bimodal composition size distribution suggesting partial vaporisation of these elements. Particle growth occurs primarily in the furnace at temperatures greater than 800°C where the alkali hydroxide vapours react with SO_2 or CO_2 and form condensed species and simultaneously the particles grow by

coagulation. Below the melting temperature of the particles, coalescence of the particles becomes slower than the particle collisions, due to increasing viscosity of the particles. Subsequently, the particles are not completely coalesced spheres but form agglomerated structures. The mean fume particle aerodynamic diameter measured at the furnace was 1.1 µm whereas it was almost 2 µm at the boiler exit. This growth is primarily due to agglomeration. The fume particles consisted mainly of Na_2SO_4 with minor amounts of $K_3Na(SO_4)_2$ and NaCl. The composition size distributions of the main species Na, K, SO_4 and Cl indicate that the particles agglomerate and sinter prior to Cl condensation on the particles, which is in agreement with the particle morphology result suggesting that the agglomeration occurs at the furnace exit. Moreover, the stage of sintering of the agglomerated fume particles depends primarily on the furnace temperature.

The mass concentration of coarse particles, i.e., of a size fraction larger than 5 µm was significantly higher than reported earlier. However, the coarse particle concentration was effected by the boiler operation and locally the concentration doubled or even tripled due to sootblowing. The particle concentration for size fraction 3–20 µm was less than 5 % of the total mass particle concentration of about 25 g/Nm^3.

The results showed two sources of coarse particles. Coarse particles formed in the furnace were efficiently depositing on the heat exchangers. The other source, which turned out to be significant as well, is the re-entrainment of particle aggregates from the heat exchangers. Four particle types could be observed to exit the furnace. The formation mechanisms of these particles could be related to progressive stages of evaporation, burning and sintering of the black liquor droplets or smelt ejecta. The particles originating in the deposits were large agglomerated particles and large irregular particles. These kinds of particles form while fume and coarse fly ash particles deposit on heat exchangers, subsequently sinter and are re-entrained spontaneously or due to sootblowing.

In conclusion, this thesis presents the fly ash formation mechanisms in recovery boilers. Moreover, the coarse particle types were identified and characterised in detail, since the novel measurement methods enabled collection of particles directly from the flue gases in recovery boiler conditions. These results can be utilised in deposit formation predictions and flue gas cleaning design.

Preface

I would like to take the opportunity of expressing my sincere gratitude to Dr. Esko Kauppinen and Dr. Jorma Jokiniemi for an inspiring research subject, and for supervising the work. Their support, guidance and knowledge during these years have been invaluable. Professor Rainer Salomaa is acknowledged for supervision during my PhD studies and especially for comments and guidance during writing of the thesis. My pre-examiners, Dr. Jorma Keskinen and Dr. Jyrki Mäkelä, I would like to thank for their contribution.

This thesis was carried out at the Aerosol Technology Group of VTT Chemical Technology. I am happy I had the opportunity to work in this group and I want to thank everybody I had pleasure to work with. Especially, I want to thank my roommate and researchmate Mr. Jouni Pyykönen for showing me that you can put your soul in your research. Dr. David Brown I thank for fruitful comments during writing of the thesis.

I dedicate my warmest thanks to all my co-authors, researchers and field personals involved in my work. Especially, I want to extend my gratitude to Ms. Inga-Lill Samuelson from ABB Power and to Professor Jim Frederick from Institute of Paper Science and Technology for sharing their vast knowledge on recovery boilers.

ABB Power, Ahlstrom Machinery, Kvaerner Pulping (former Tampella Power), Walter Ahlström’s Foundation, Ministry of Trade and Industry and TEKES via LIEKKI and SIHTI-programmes, and VTT Chemical Technology are gratefully acknowledged for funding this work.

Finally, I am deeply touched by the patience, support and understanding my husband Jussi and sons Alfons and Arttu have shown throughout this work. I want to thank the rest of my family and friends for their encouragement.

Pirita Mikkanen

Tampere, June 2000

Contents

Appendices

Appendices of this publication are not included in the PDF version.
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List of symbols

A	chemical activity coefficient
C	concentration of species Na, K, S or Cl
D_{aggl}	characteristic diameter of agglomerate
D_f	fractal dimension
D_p	particle diameter
D_v	vapour diffusion coefficient
D_0	diameter of primary particle
ER	enrichment factor
k_v	heat conductivity of vapour
K	coagulation coefficient for monodisperse particles of size R_p
Kn	Knudsen number
L	latent heat of condensation
M_g	molecular mass of gas
M_v	molecular mass of vapour
N	number concentration of particles
N_0	number of primary particles
p_g	gas pressure
$p_{v,\infty}$	actual vapour pressure in free stream
$p_s(T_\infty)$	equilibrium vapour pressure in free stream
R	gas constant
R_p	particle radius
S_{Rp}	saturation ratio over curved surface
S_∞	saturation ratio
t	time
t_c	characteristic time
T_g	gas temperature
T_p	particle temperature ($\approx T_\infty$ for fine particles)
T_∞	gas temperature in free stream
β_M, β_T	transitional correction factors for mass and heat transfer
σ_l	surface tension of condensed vapour on particle
σ_p	surface tension of particle
ρ_l	density of condensed vapour
ρ_p	particle density
μ	gas viscosity
μ_p	particle viscosity

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A. Mikkanen, M. P., Kauppinen, E. I., Jokiniemi, J. K., Sinquefield, S. A. and Frederick, W. J. 1995. Bimodal fume particle size distributions from recovery boiler and laboratory scale black liquor combustion. Tappi Journal, Vol. 77, No. 12, pp. 81–84.

B. Jokiniemi, J. K., Pyykönen, J., Mikkanen, P. and Kauppinen, E. I. 1996. Modeling fume formation and deposition in kraft recovery boilers. Tappi Journal, Vol. 79, No. 7, pp. 171–180.

C. Mikkanen, P., Kauppinen, E., Pyykönen, J., Jokiniemi, J. and Mäkinen, M. 1997. Alkali salt ash formation during black liquor combustion at kraft recovery boilers. In: Applications of Advanced Technology to Ash-Related Problems in Boilers, (Eds.) Baxter, Larry and DeSollar Richard. Engineering Foundation Conference, Waterville Valley, USA 16–21 July 1995. Pp. 409–423.

D. Mikkanen, P., Kauppinen, E. I., Pyykönen, J., Jokiniemi, J. K., Aurela, M., Vakkilainen, E. K. and Janka, K. 1999. Alkali salt ash formation in four Finnish industrial recovery boilers. Energy and Fuels, Vol. 13, pp. 778–795.

E. Mikkanen, P., Jokiniemi, J. K., Kauppinen, E. I. and Vakkilainen, E. K. 1998. Experimental and modelling study on the fume formation at a Kraft recovery boiler. Accepted for publication in the AIChE Symposium Series.

F. Mikkanen, P., Jokiniemi, J. K., Kauppinen, E. I. and Vakkilainen, E. K. 1999. Coarse ash particle characteristics in a pulp and paper industry chemical recovery boiler. Submitted for publication in Fuel.

G. Mikkanen, P., Jokiniemi, J. K., Kauppinen, E. I. and Vakkilainen, E. K. 2000 Deposit formation study at an operating recovery boiler. Submitted for publication in Fuel Processing Technology.

This thesis has been carried out at the Aerosol Technology Group of VTT Chemical Technology during the years 1992–2000 under the supervision of Dr. Esko I. Kauppinen and Dr. Jorma K. Jokiniemi.

The work was initiated with industrial scale experiments applying measurement methods adapted from pulverised coal combustion studies (Paper A). The measurements were carried out at the boiler exit at about 150°C. However, the methods suitable for the pulverised coal combustion studies required modifications in order to be applied to recovery boiler conditions. The confronted problems and solution in dilution and coarse particle sampling are described in Papers C and D. Furthermore, the first studies indicated that coarse particles deposited efficiently on the heat exchangers and that re-entrainment of particles took place. Thus the measurements were carried out prior to the heat exchangers - at the recovery boiler furnace at about 900°C or at the superheater area at about 750°C. Altogether, the extensive ash formation studies were carried out in five operating recovery boilers in Finland. The results of the experiments carried out with improved measurement methods upstream and downstream of the heat exchangers are described in Papers D–G.

Papers A, C, D, F and G are based on the author's experimental work at industrial scale recovery boilers and in the laboratory. The laboratory scale experiments, described in Paper A, were carried out in co-operation with Professor Jim Frederick and Dr. Scott Sinquefield during the author's stay at the Oregon State University, in 1993. In Paper C, the results were interpreted in co-operation with Mr. Jouni Pyykönen. For Papers D, F and G, the author of this thesis was responsible for the experiments, conducted the data analysis, interpreted the results and wrote the papers.

In addition to the experimental part of the work, gas-to-particle conversion was studied with an Aerosol Behaviour in Combustion (ABC) model. The ABC model utilised in this study includes models for fume particle formation and growth by condensation, coagulation and chemical reactions, as well as models for deposition. Applying the ABC model to recovery boilers is introduced in Paper B and the results of the recovery boiler simulations are compared with the measured ones in Paper E. The author responsible for Paper B was Dr. Jorma K. Jokiniemi. The author of this thesis produced the experimental data and participated in the interpretation of the results. The author carried out the recovery boiler experiments and ABC code simulations and wrote Paper E.

Dr. Kauko Janka and Dr. Esa Vakkilainen were the representatives of the recovery boiler manufacturers. Ms. Minna Aurela carried out the ion chromatography analysis.

1. Introduction

Black liquor, the waste sludge from the paper pulping process, is burned in recovery boilers where the pulping chemicals are recycled and heat from burning of the organic matter is utilised for producing electricity and steam. To a large extent, due to recovery boilers, pulp and paper mills are energy self sufficient, or in modern mills they even produce excess electricity. Almost 7% of the primary energy in Finland was produced in recovery boilers in 1997. In addition to energy production and recycling of pulping chemicals, recovery boilers can be utilised for the destroying of other wastes, e.g. sludges from biological water treatment, or the odorous gases from the pulping process. Moreover, since black liquor originates from wood, it is considered to be biomass. The biomass fuels can be regarded as CO_2 neutral fuels, because they consume roughly the same amount of CO_2 during photosynthesis as is released during combustion (Vakkilainen, 1998).

Due to the energy demand of pulp and paper mills and, on the other hand, strict environmental regulations there is a need for higher efficiency in the recovery boilers. This could be achieved by increasing the temperature and pressure of the primary steam. Currently, typical steam temperature in the recovery boiler is about 480°C and pressure 10 MPa, whereas in pulverised coal combustion boilers the corresponding values are about 550°C and 15 MPa. However, increased steam temperature increases the risk of corrosion and of thickened deposit layers. The thickened deposit layers may decrease boiler efficiency and, in the worst case, cause a boiler shutdown due to deposit layers that plug the flue gas channel. Particularly in recovery boilers, where the fly ash concentration in the flue gas is as high as 10–25 g/Nm^3, deposit formation can be very rapid. Recovery boiler fly ash consists mainly of sodium and potassium salts, which have relatively low melting temperatures. In addition, the trend of closing the process water circuits accumulates potassium and chlorine in the recovery cycle, which causes fly ash composition with even lower melting temperatures (Hupa et al., 1998).

The high fly ash concentration in flue gas is a challenge to the flue gas cleaning technology mainly to the electrostatic precipitator (ESP) and the flue gas scrubber. In many gas-cleaning devices, the fly ash capture efficiency is the poorest for particles in the size range 0.1–1 µm (Flagan and Seinfield, 1988).

Unlike in other solid or sludge firing boilers, in recovery boilers the main fraction of fly ash particles exists in this size range. Furthermore, the fly ash particles in recovery boilers are hygroscopic. This can cause sintered layers of particles inside the gas-cleaning device, which deteriorate the device performance.

On the other hand, the high particle concentration in the recovery boiler can have advantages, because of the efficient capture of SO_2 in the flue gas. Modern design and improved boiler operation has increased the combustion performance, which often means higher furnace temperatures. Sodium species, which are the main SO_2 captures, evaporate more efficiently in high furnace temperatures. This causes increased particle concentrations in flue gases. Consequently, the SO_2 emissions have decreased from a typical value of 500 ppm in 70's close to zero in modern boilers. Simultaneously, the total reduced sulphur and carbon monoxide emissions have decreased significantly.

The aim of this thesis has been to develop measurement methods for recovery boiler conditions in order to obtain detailed information on fly ash particle characteristics such as particle morphology, size and composition. With these characteristics and utilising knowledge on aerosol dynamics, included for example in the Aerosol Behaviour in Combustion (ABC) code, the formation and growth mechanisms of the fly ash particles can be demonstrated. These results can be applied to solve the problems in the deposit formation and growth as well as in the gas-cleaning technology.

The thesis begins with a short review of recovery boilers. The characteristics of the black liquor as a fuel and the recovery boiler design are discussed briefly along with a description of fly ash particle composition in recovery boilers. Since earlier fume formation theories discuss mainly the chemistry of the particles but overlook the theory of particle formation and growth, the major phenomena in fine fly ash particle formation and growth via gas-to-particle routes are presented. These are followed by a general description of coarse fly ash particle formation via mechanical phenomena.

Next, sampling methods and measurement devices are described. Uncertainties in the measurements are discussed, based on results of measurement repetitions and on estimates of the maximum errors caused by non-optimal sampling. Then the novel characterisation methods are introduced. Experimental methods are followed by description of simulations with ABC model.

Finally, the main results of Papers A–G are discussed in detail. The fume particle formation and growth mechanisms are presented. Furthermore, the comparison of the experimental and the modelling results show that it is possible to predict fume particle characteristics in the recovery boiler flue gas. In addition, the coarse particle formation mechanisms are proposed based on their physical appearance and composition.

2. Black liquor combustion in recovery boilers

2.1 Black liquor as a fuel

Black liquor is a by-product of the pulping process. It contains about half of the wood processed in pulping along with the pulping chemicals. Characteristics of black liquor depend on the raw material, i.e. wood, the pulping process and methods of black liquor drying. Nevertheless, prior to combustion, typical black liquor consists of about one third pulping chemicals, one third biomass and one third water (e.g. Heiningen et al., 1992). A higher heating (gross calorific) value of the black liquor is typically 13.4–15.5 MJ/kg (Frederick, 1997).

Due to the main pulping chemicals NaOH and Na_2S there is typically 20 % sodium content in black liquor dry solids. As a consequence of the main pulping chemicals, Na and S are called process elements in black liquor. In Scandinavian liquors, the sulphur content is relatively high – about 5–6% – as compared with the North American liquors (circa 3%). The concentration of non-process elements K and Cl varies mainly due to raw material and accumulation of these species in the process. For instance, coastal North American liquors contain up to 2–3 % of chlorine, whereas the highest Cl contents in Finland are about 1% in the dry solids of the combustion black liquor. In any case, only a fraction of Na, K, S and Cl is volatilised in the recovery boiler furnace, the rest is recycled.

Most of the heat during the black liquor combustion is produced by biomass burning. The main organic constituents in the black liquor are lignin and aliphatic carboxylic acids. These, among other biomass compounds in the black liquor, are reported to have clear influences on the black liquor combustion properties (Alen and Siistonen, 1998). The aliphatic carboxylic acids effect the early stages of combustion, while the lignin concentration affects the swelling and char burning of a black liquor droplet, that is the later stages of combustion.

Black liquor is dried prior to combustion, traditionally to a 55–60% dry solids content and, with advanced techniques, to about 80%. Simultaneously, with improved boiler operation practice, the combustion of black liquor with high dry solids content has increased energy recovery, decreased SO_2 and reduced sulphur emissions, and increased volatilisation in the furnace (Karvinen et al., 1991; Vakkilainen et al., 1999). Moreover, water in the liquor is the main water vapour source in the recovery boiler furnace, thus, due to increasing dry solids content in the black liquor, the water content in the flue gas has decreased over the years.

2.2 Black liquor combustion in recovery boilers

In the recovery boiler furnace, the organic matter in the black liquor is burned and the inorganic elements are recycled for further use in the pulping process. A modern recovery boiler can burn 3 000 tons of black liquor per day. The hot flue gas from combustion exits the furnace into the convective heat transfer section of the flue gas channel (Figure 1). In this section, the heat from the flue gas is transferred to the water and steam in heat exchangers. The hottest area of the convective section is called the superheater area and the other sections boiler bank or generating bank and economisers. The heat exchangers are continuously cleaned with sootblowing.

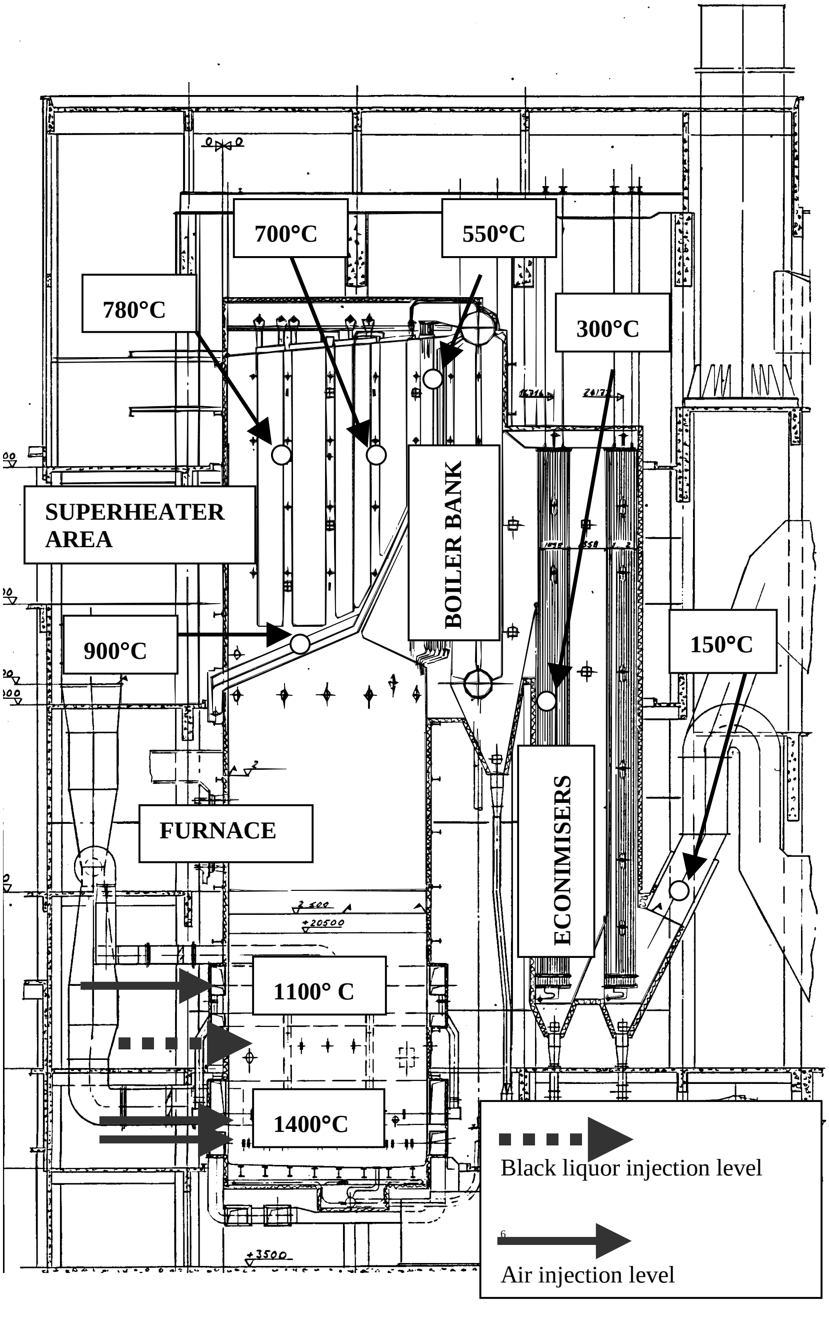

Figure 1. Schematic of a recovery boiler with typical flue gas temperatures firing 1700 tons of dry solids per day. The boiler height is about 40 m and the hearth area about 80 m^2.

The recovery boiler furnace operates with multiple nozzles, which spray the black liquor into the furnace as droplets of about 1–5 mm in diameter. The droplets dry, swell during devolatilisation of organic volatiles, and burn (Macek, 1999; Hupa et al., 1985; Saastamoinen, 1995; Alen and Siistonen, 1998; Verrill and Nichols, 1998). Most of the burning droplets are deposited on the smelt bed on the bottom of the furnace but some droplets are entrained from the furnace to the heat exchanger part of the flue gas channel. The droplets deposited on the smelt bed form a burning char layer on top of the molten salt. The entrained particles are called carryovers.

Recovery boilers operate with multiple combustion air levels. The combustion air is usually introduced to the furnace at three to five vertical levels (Jones, 1997; Jones and Chen, 1995; Vakkilainen et al., 1998; Wessel et al., 1998a). On the lowest part of the furnace, primary air is blown from a large number of air ports located on all four furnace walls. Primary air pushes the bed away from the walls and maintains a proper bed temperature as well as a reactive char layer on top of the smelt. Secondary air may be divided in several levels and walls of the furnace. Secondary air has a great influence on the flow pattern and consequently on the combustion performance. The purpose of tertiary, or quaternary air, is to burn the possible carryovers and to complete the mixing of the flue gases before they exit the furnace.

Because of the smelt bed on the bottom and the black liquor spray in the low part of the furnace as well as the levelled combustion air injection, the vertical and horizontal flue gas characteristics vary significantly. In the lowest part of the furnace, oxygen is consumed by char combustion on the top of the smelt bed; thus the conditions can be reducing. From the black liquor spray in the lower part of the furnace, large quantities of water vapour and organic volatiles are released. Below the liquor spray level, where most of the volatile combustion occurs, the gas temperature is at its highest: about 1300–1400°C in a modern boiler (Jones and Chen, 1995; Wessel et al., 1998b). The flue gas temperature decreases to about 1100°C at the high secondary air level. Typically, the furnace exit temperature, i.e. the temperature upstream of the superheaters, is about 900°C (e.g. Jones and Chen, 1995; Vakkilainen et al., 1998; Wessel et al., 1998b; Walsh et al., 1998). A modern recovery boiler with typical flue gas temperatures is shown in Figure 1.

2.3 Fly ash chemistry in recovery boilers

In the recovery boiler furnace, a fraction of inorganic species in the black liquor is volatilised. These elements include Na, K, S, Cl, and C, which form condensable compounds in the flue gas. Unlike in most combustion processes, in the recovery boiler the concentration of particles smaller than 5 µm in diameter is very high about 10–15 g/Nm^3 (Bosch et al., 1971; Nguyen and Rowbottom, 1979; Hood 1980). These particles, formed from vaporised species, are called fume particles. The main component in the recovery boiler fume particles is Na_2SO_4. In addition, there are typically carbonates, 2–10% NaCl and 5–30% K_2SO_4 and KCl (Tran, 1986; Hupa et al., 1998; Lien et al., 1999).

Lang et al. (1973) suggested the earliest fume formation theory for recovery boilers. He proposed that fume formation is initiated by decomposition of Na_2CO_3 in the char bed to Na_2O, which further reacts above secondary air level with SO_2 or CO_2 to form Na_2SO_4 or Na_2CO_3, respectively. However, there is water vapour present in the recovery boiler furnace and thus sodium favours conversion to NaOH (Hynes et al, 1984; Srinivasachar et al., 1990).

Later Cameron (1986, 1987) proposed a reaction-enhanced mechanism of fume formation. According to him, sodium is released from the char bed as sodium vapour, which reacts with oxygen and carbon dioxide to form Na_2CO_3. Since Na_2CO_3 is not stable in the vapour phase, the particles are formed instantaneously. He concluded that the Na_2CO_3 particles are formed close to the char bed and further react with SO_2 to form Na_2SO_4. However, as discussed earlier, the furnace temperature most likely exceeds the decomposition temperature of Na_2CO_3 and thus these particles would decompose.

Modelling of fume formation has been carried out in the context of studies of inorganic species release from black liquor in laboratory conditions or during boiler experiments. In these models, the total or local released concentrations of inorganic species have been introduced to multiphase chemical equilibrium calculation, which describes the chemistry and phases of particle forming species, or to a model considering even the chemical kinetics (Hupa et al., 1998; Wessel et al., 1997, 1998; Verrill et al., 1998; Wåg et al., 1997). However, both these approaches neglect the mass transfer dynamics during fume particle formation. Consequently, these models cannot predict fume particle number, mass and composition size distributions in detail.

Carryover particles deposit efficiently on the heat exchangers and thus they are seldom detected in the boiler exit, i.e. upstream of the gas cleaning devices. In the superheater area, carryover particle concentration and composition have been calculated based on deposition probe measurements (e.g. Backman et al., 1987, 1995; Tran et al., 1983, 1985). In this method, a water and/or air-cooled probe is inserted into the flue gas channel and the deposit accumulation in the front and the backside of the probe is measured and analysed for chemical composition. It has been assumed that the deposit on the front side consists of coarse particles and the deposit on the backside represents fume particles. The carryover particle concentrations measured with this method have been 1–7 g/Nm^3 in the superheater area (Backman et al., 1995). Typically, the carryover particles have been reported to consist of 20–45% Na_2SO_4, 50–70% Na_2CO_3, 2–5% NaCl, 0.3–0.6% Na_2S and some unburned organic material (Tran, 1986; 1987; Hupa et al., 1998).

Often it is more convenient to calculate the ratios of concentrations of elements in particles ($C_{in\ fume}$) and in black liquor ($C_{in\ black\ liquor}$) than to calculate a mass balance over the entire recovery boiler. The ratios are presented as an enrichment factor ER_{ij}. The enrichment factor of species i versus species j is calculated according to Equation 1 (Reeve, 1981).

$$ER_{ij} = \frac{C_{i,in\ fume} / C_{j,in\ fume}}{C_{i,in\ black\ liquor} / C_{j,in\ black\ liquor}}, \quad \mathrm{i, j = Na, K, S, Cl} \qquad (1)$$

Since only a fraction of Na, K, S and Cl is released during combustion, the enrichment factor describes the volatility of these elements.

3. Combustion aerosol formation and growth

As discussed above, former fume formation theories have generally overlooked the dynamics of particle formation and growth via gas-to-particle routes. In the following, these phenomena during the fume formation in the recovery boilers are discussed briefly.

A combustion aerosol is a dynamic mixture of gases, vapours and particles in a flue gas. Usually, the gas composition is expressed in terms of volumetric fractions, the vapour content is given as vapour pressures of each condensable compound and the particle characteristics are represented as size distributions and morphologies. The size distributions are presented as a concentration of a given property - number, mass or composition - versus particle size. The particle size can be expressed as an aerodynamic particle diameter assuming a spherical particle with a reference density of 1 000 kg/m^3 (c.f. Hinds, 1998). In this thesis, most of the particle sizes are reported as aerodynamic diameters.

Since the flue gas temperature decreases from over 1 400°C to about 150°C, a dimensionless number relating the particle diameter (D_p) to the mean free path (λ_g) of gas molecules is introduced. This number called Knudsen number Kn is calculated as (c.f. Flagan and Seinfield, 1988)

$$Kn = \frac{2\lambda_g}{D_p}$$

$$\lambda_g = \frac{\mu}{0.499\, p_g \sqrt{\dfrac{8M_g}{\pi R T_g}}} \qquad (2)$$

where μ is the gas viscosity, p_g is the gas pressure, M_g is the molecular weight of the gas, R is the gas constant and T_g is the gas temperature.

For very small particles (Kn >> 1), the kinetic theory of gases applies and the particles are said to be in free molecular or kinetic regime. In contrast, for large particles (Kn <<1), continuum mechanics apply and the particle is said to be in continuum regime. The region in between these two is called the transition region (c.f. Seinfield and Pandis, 1998).

Often, in combustion processes, particles formed by gas-to-particle conversion stick together and form agglomerates. The compactness of the agglomerated structures can be described with a fractal dimension (D_f). The fractal dimension for a straight chain of particles is 1 and for compact spherical structure 3 (for more details see Hinds, 1998). The fractal dimensions of fly ash particles are often between 1.3 and 2.2 (Baron and Willeke, 1993; Ludlow and Vosen, 1993; Hueglin et al., 1997; Fang et al., 1998). The following relation between number of primary particles in an agglomerate (N_0), primary particle size (D_0), and a characteristic diameter of an agglomerate (D_{aggl}) can be derived (Lehtinen, 1997).

$$N_0 \approx \left(\frac{D_{aggl}}{D_0} \right)^{D_f} \tag{3}$$

3.1 Homogeneous and heterogeneous nucleation

Condensation of a vapour can take place when its saturation ratio (S_∞) exceeds one;

$$S_\infty = \frac{p_{v,\infty}}{p_s(T_\infty)} \tag{4}$$

where $p_{v,\infty}$ is the partial pressure of the vapour in flue gas and $p_s(T_\infty)$ is the saturation vapour pressure.

If, as a result of rapid cooling or chemical reactions, the saturation ratio of a vapour exceeds one, the vapour is said to be supersaturated. In some cases, the saturation ratio is high enough for new particle formation from vapours. This phenomenon is called homogeneous nucleation or homogeneous condensation (c.f. Flagan and Seinfield, 1988). Heterogeneous nucleation occurs on a surface of a pre-existing particle (c.f. Jokiniemi et al., 1994).

Homogeneous nucleation may occur in the boundary layer of a combusting particle or surface. For example, some metals can vaporise due to a local reducing atmosphere. However, once these reduced compounds are oxidised in the combustion boundary layer they have very low equilibrium vapour pressures and homogeneous nucleation of oxidised metal compounds occurs (e.g. Senior and Flagan, 1982; Helble et al., 1986). Similarly, supersaturation may occur due to a thermodynamically favoured chemical reaction during flue gas cooling. This is the case in the sulphation of sodium hydroxide vapours in flue gas.

3.2 Growth by condensation and chemical reactions

Particles may further grow by condensation of vapours on pre-existing particles. For very small particles (Kn>>1) condensation is governed by the rate of random molecular collisions of vapour molecules with particles, whereas for coarse particles (Kn<<1) condensation occurs via diffusion (cf. Flagan and Seinfield, 1988). In the transition region ($Kn \approx 1$), a general solution valid over the full range of Knudsen numbers does not exist. The growth of the particles due to vapour condensation can be calculated by the Mason equation (5), where both mass and heat transfer limitations are taken into account (Williams and Loyalka, 1991; Jokiniemi et al., 1994). The terms for mass transfer N_M and heat transfer N_T depend on properties of particles (ρ_p the particle density), vapours (L the latent heat of condensation, M_v the molecular mass of vapour, D_v the diffusion coefficient for vapour, $p_s(T_\infty)$ the equilibrium vapour pressure in free stream, k_v the heat conductivity of vapour) and flue gases (R the gas constant, T_∞). β_M and β_T are correction factors for mass and heat transfer, respectively.

$$R_p \frac{dR_p}{dt} = \frac{S_\infty - S_{R_p}}{\frac{N_M}{\beta_M} + \frac{N_T}{\beta_T}} \tag{5}$$

$$S_{R_p} = Ae^{\left(\frac{\sigma_l M_v}{2 R_p R \rho_l T_p}\right)}$$

$$N_M = \frac{\rho_p R T_\infty}{D_v \, M_v \, p_s(T_\infty)}$$

$$N_T = \frac{\rho_p L^2 \, M_v}{k_v \, R T_\infty{}^2}$$

In the saturation ratio on the curved particle surface (S_{Rp}), the Kelvin effect and formation of solutions can be taken into account. The Kelvin effect, caused by a higher vapour pressure over a curved surface than over a flat surface, is introduced by the exponential term in S_{Rp}. Likewise, the chemical activity coefficient (A) represents the effect of solutions on the vapour pressure on the particle surface (c.f. Flagan and Seinfield, 1988).

The Mason equation (equation 5) describes the condensation to a spherical particle. However, in the combustion processes the particles are generally agglomerates in the convective path. For the very fine agglomerates the distribution of condensed species among various particle sizes does not depend on the diameter of agglomerate (D_{aggl}; equation 3), only upon the size of the primary particles. In contrast, for the coarse agglomerates (Kn <<1) the concentration of condensed species depends on the shape and density of the agglomerate (Lind, 1999). However, if the diffusion within the agglomerate limits the condensation, there is no simple approximation yet available (Rosner and Tandon, 1994).

Chemical reactions of condensed species with vapour species can also be involved in the gas-to-particle conversion process. In this case, particle growth can be, besides diffusionally controlled, surface reaction controlled or volume reaction controlled or a mixture of these. The rate controlling phenomena in a surface reaction controlled process is the rate of surface reaction involving the adsorbed vapour molecule. In the volume reaction controlled process, the rate is controlled by the rate of reaction involving the dissolved species occurring within the particles.

3.3 Growth by agglomeration

Simultaneously with condensation, particles collide with one another. As a result of the collisions the particles usually stick together and form larger particles i.e. coagulate. The collisions can occur due to Brownian motion when the process is called Brownian coagulation, or due to external forces, such as gravity, electrical forces or fluid dynamics, when the process is called kinematic coagulation. During coagulation, the number concentration (N) of monodisperse particles decreases in proportional to the coagulation coefficient (K), which depends on particle sizes and flue gas properties (for more details see Seinfield and Pandis, 1998). Brownian coagulation is at its slowest for monodisperse particles (c.f. Fuchs, 1964; Seinfield and Pandis, 1998).

$$\frac{dN}{dt} = -K\,N^2 \qquad (6)$$

When the particles collide and coalesce to spherical form, the process is called coagulation. However, in the combustion processes agglomerates may form due to particle collisions that are faster than the particle coalescence. Then the collision and sticking process is called agglomeration. The time for the complete coalescence of two particles via surface tension σ_p and viscous flow can be expressed (Ulrich and Subramanian, 1977) as

$$t_c = \frac{\mu_p\,D_p}{2\sigma_p} \qquad (7)$$

As discussed earlier, the agglomerated structures are described by the fractal dimension D_f (Equation 3). The lower the fractal dimension the higher the coagulation coefficient is (Rogak and Flagan, 1992). Furthermore, electrical and radiative forces can affect Brownian coagulation coefficient. Normally, aerosol particles do not carry high electrical charges. However, even trace amounts of alkali metals in flames can introduce very high ion concentrations. This, in turn, can charge the particles, which has been observed to suppress the coagulation of e.g., soot particles in flames (Haynes et al., 1981). Likewise, even though the fine particles are normally in thermal equilibrium with the flue gases, the particles may emit or absorb radiation in the presence of hot flames or cold heat exchanger surfaces. The radiation can cause a temperature difference between gas and particles, which can alter the coagulation coefficient. According to theoretical studies by Mackowski et al. (1994), under conditions of radiative cooling, e.g. in the presence of cold heat exchanger surfaces, the growth of relatively coarse (≈ 2 µm) spherical particles by Brownian coagulation can be enhanced significantly. The importance of these phenomena in combustion processes, however, is not yet properly understood.

Agglomerates formed from the primary particles tend to partly coalesce together due to the difference in free energy or chemical potential between the neck area and the surface of the particle. This is called sintering (Kingery, 1976). At some point, the particle collisions may occur so seldom, that the agglomerate growth by collisions is negligible and the major restructuring process is sintering. As agglomerate with a fractal dimension larger than 2 sinters, the fractal dimension increases and approaches the value 3 (Tandon and Rosner, 1996). The characteristic times for complete coalescence derived from the initial stage sintering models for viscous flow, evaporation-condensation, lattice diffusion, surface diffusion, and grain boundary diffusion (Ulrich and Submaraniam, 1977; Lehtinen, 1997) indicates that coalescence takes longer for larger particles.

3.4 Coarse particle formation

In very general terms, the formation of coarse particles in combustion is governed by mechanical transformations of inclusions in fuel or incomplete burning products. As an example, the coarse particle formation in heavy oil and in pulverised coal combustion is discussed. During heavy oil combustion, the fuel is sprayed into furnace in small droplets, whereas during pulverised coal combustion fine coal particles are fed into the furnace with carrier gas. Nevertheless, there are similar coarse particle characteristics detected in both processes (Lawn, 1984; Flagan and Seinfield, 1988). Coke spheres are porous spherical particles that have blowholes on surface. This kind of particles are seldom detected in the convective section of the modern boilers. More likely, the coke spheres continue burning with increasing density until they fragment in later stages of burning. The fragments may include pieces of mineral matter originating from the parent fuel. These mineral inclusions may come into contact within the burning fragment and form large agglomerates or solid spheres. The fragmentation of fuel particles or droplets may occur during rapid heating while the fuel particle is being inserted into the furnace, as well. Cenospheres are formed from a vaporising fuel particle or droplet that bursts open from the internal release of gases and subsequently partly or completely closes due to surface forces.

In addition to the coarse particles formed in the furnace at different stages of the combustion process, coarse particles may form due to entrainment of material from the deposit layers at the heat exchangers. Since the deposit layer decreases the heat transfer from the flue gas to the steam, it is periodically removed from the heat exchangers by sootblowing. In the recovery boilers, the sootblowing is continuously operated around the flue gas channel whereas in utility boilers sootblowing can be carried out only once a day. Most of the particles detached during sootblowing are too large to follow the flue gas flow, but some may contribute to the coarse particle fraction of the fly ash. Moreover, re-entrainment of deposited particles can also occur spontaneously due to flue gas flow (Matsusaka and Masuda, 1996).

4. Experimental and modelling methods

4.1 Experimental methods

The experimental part of this thesis was carried out at five industrial recovery boilers in Finland. The experiments were carried out at Veitsiluoto Oulu in 1992, at Metsä-Botnia Kemi in 1993, at UPM-Kymmene Kaukas in 1995, at UPM-Kymmene Kuusankoski 1996 and at UPM-Kymmene Wisaforest in 1998. These five boilers were chosen primarily because of the following features. Veitsiluoto Oulu mills recovery boiler periodically fires pure softwood and pure hardwood liquor. Metsä-Botnia Kemi mills recovery boiler was chosen because of its advanced evaporator technique, which can increase the black liquor solids content up to about 85%. At UPM-Kymmene Kaukas mills recovery boiler the effect of 30% overload was tested. UPM-Kymmene Kuusankoski mills recovery boiler was a traditional boiler operated since 1977. UPM-Kymmene Wisaforest mills recovery boiler was renovated two years prior to the experiments and had a chlorine content of 0.5% in the black liquor.

4.1.1 Measurement methods

The main goal of the experiments was to measure particle characteristics (Table 1) at the recovery boilers. The samples were collected in the furnace at a flue gas temperature of about 900°C or in the superheater area at about 750°C and at the boiler exit, i.e., upstream the electrostatic precipitator, at about 150°C (see Figure 1). In Table 1, the particle characteristics, the measurement methods including the sample extraction system and the measurement devices, as well as the analysis methods, are shown. Brief descriptions of these follow. The schematics of the experimental setups at different recovery boilers are presented in Figure 1 of Paper D, Figure 1 of Paper E, Figure 2 of Paper F, and Figure 2 of Paper G.

Table 1. Particle characteristics, measurements methods and analyses methods.

Particle characteristics	**Measurement method**	**Analysis methods**
particle mass concentration	cyclone-filter double cyclone-filter three-stage cyclone	gravimetric
particle overall composition	cyclone-filter double cyclone-filter	ion chromatography (IC)
number size distribution	dilution-cyclone-differential mobility analyser with condensation nucleus counter	
particle mass size distribution	dilution-low pressure impactor	gravimetric
composition size distribution	dilution-low pressure impactor	IC inductively coupled plasma mass spectrometry (ICP-MS)
fine particle morphology	thermophoretic sampler filter low pressure impactor	scanning electron microscope (SEM) transmission electron microscope (TEM)
coarse particle morphology	settling probe double cyclone cyclone-low pressure impactor	SEM TEM
coarse particle composition	cyclone	energy dispersive X-ray analyses (EDX) computer controlled scanning electron microscopy (CCSEM)
particle crystallinity	cyclone-low pressure impactor	X-ray diffraction (XRD) TEM
occurrence of chemical compounds in particles	cyclone	X-ray absorption fine structure spectroscopy (XAFS)

Since the gas temperature and the particle concentration were high, some of the samples were extracted from the flue gas flow with a dilution system (Table 1). Three kinds of dilution systems were used. In our first studies, the sample was diluted with an ejector type dilutor (Koch et al., 1988). In this system, the coarse particles were collected from the flue gas flow prior to the dilutor with a sampling cyclone. The cyclone samples were further size classified in order to achieve coarse particle size distribution. However, because the size classification of the cyclone samples was unsuccessful for recovery boiler fly ash (Paper C) and because of deposition problems in the ejector type dilutor, an axial dilutor was designed (Paper D). The axial dilutor was applied at the boiler exit at about 150°C (Papers D–F). The third dilutor type was applied during sampling at the boiler furnace at about 900°C and at the superheater area at about 750°C (Papers D and E). At these temperatures, the sample was quenched with a porous tube dilutor to avoid further reactions of the flue gas and to nucleate the vapour phase species.

A pre-cyclone (Papers A, C–E) and a double cyclone (Paper F) system were used to collect the coarse particles. The size of the particles collected with the cyclone can be expressed in terms of an aerodynamic cut-size which depends on the sample gas flow rate and viscosity (Lee et al., 1985).

The particle concentration measurements were carried out with quartz fibre filters. These filters have a large capacity and a low pressure drop but they may react with sulphur compounds, especially at high temperatures (Papers D–F). The planar polycarbonate filters were used to collect particles for morphology studies (Papers C–E).

The number size distributions of the particles from 0.01 µm to 0.8 µm in diameter were determined with a differential mobility analyser (DMA) coupled with a condensation nucleus counter (CNC)(Knutson and Whitby, 1975; Hoppel, 1978; Reischl, 1991; Papers B and E). The DMA size classifies particles according to their electrical mobility and the number concentration in each size class is counted with the CNC.

Mass and composition size distributions of the particles in the size range 0.02–16 µm in aerodynamic diameter were measured with the Berner type low pressure impactor (BLPI)(Berner, 1980; Kauppinen, 1992; Papers A–F). The BLPI size classifies the particles according to their aerodynamic diameter into eleven size classes. The samples in these size classes are weighted for the mass size distribution, and analysed for elemental concentrations for the composition size distribution. In addition, each size class can be studied with electron microscopy for the particle morphology.

For electron microscopy analyses, a particle sampler, in which a cooled copper grid collects particles by thermophoresis (T-SEM), was designed (Papers C–D, F–G). The grid is continuously flushed with cooling air when inserted into the furnace. The flushing is interrupted for a sampling time of 5 to 10 s. The collection efficiency is relatively insensitive to particle size and morphology for particles smaller than about 1 µm and decreases for larger non-agglomerated particles, due to an internal temperature gradient (Talbot et al., 1980).

The individual coarse particles were collected for morphology and cross section studies with a settling probe (Paper F). In this probe, particles are collected in three stages. In the probe head, the largest particles, over 500 µm in size, hit an impaction plate as the sample flow turns 90°. Simultaneously, the sample flow velocity decreases so that a laminar flow in the settling chamber is achieved. In the laminar flow, the particles 50–500 µm in size settle on stainless steel stripes, which are placed on the bottom of the chamber (Hinds, 1998; Bürkholz, 1995).

The device applied for deposit growth rate studies was a water and air cooled tubular probe with regulated surface temperature (Tran et al. 1983; Hupa et al., 1998). The deposit sample cross sections were studied for layer thickness and porosity with electron microscopy (Paper G).

4.1.2 Uncertainties in the measurements

The uncertainties in the measurement methods are threefold. Firstly, extraction of the sample from the flue gas flow may cause an error. A choice of the sampling location can be included in this factor (c.f. Calvert and Englund, 1984; Brockmann, 1993). Secondly, dilution or transport of the sample within the measurement system may change the sample properties or cause losses (Brockmann, 1993). Thirdly, the measurement device may cause an error.

The major uncertainty in the recovery boiler measurements arises from the unstable combustion condition in the recovery boiler furnace. The instability causes uneven flow patterns within the furnace or on the cross section of the flue gas channel. This can be detected as a maximum temperature difference of even a few hundred degrees between opposite sides of the superheater inlet. Moreover, the instability causes continuous pressure and gas velocity changes.

For example, the gas flow can change from 4 to 8 m/s and back in 20 minutes in the boiler bank area (Tran et al., 1985).

The errors caused by the unstable combustion conditions cannot be easily avoided. However, the experiments for this thesis included short-term sampling as well as continuous and integrating methods (Paper C). The continuous measurements and information from the boiler control system were utilised in selecting the most representative sampling times and sites as well as in observing the state of combustion in the furnace. Furthermore, the fine particle sampling is less sensitive to the unstable flue gas flow than the coarse particle sampling is. In fact, the measurement results for the fine particle size distributions were repeatable within 10%. Moreover, since the coarse particle results are most sensitive to the unstability in combustion conditions, most of the results are presented semiquantitatively.

The sampling losses in the sampling lines were minimised by decreasing the sampling line length and avoiding a temperature difference between the sample and the sampling line surfaces. However, during the furnace sampling cooling air channels ruptured and the designed cooling rate of the sample was not achieved, thus thermophoretic losses in the sampling lines were significant (Paper D). The boiler exit measurements were carried out primarily within the flue gas channel. At some sampling sites, the boiler ports were too small for the sampling devices hence the equipment was placed outside the flue gas channel. To avoid thermophoresis in these sites the sampling lines, the devices and the dilution gas were heated to the flue gas temperature.

The estimates for the maximum losses in the sample system inlet, in the sampling lines, and during measurement with the cyclone-ejector dilutor system are shown in Figure 2. The losses in the sampling system inlet by misalignment and by non-isokinetic sampling are calculated according to Hinds (1998). The effect of transport losses by diffusion and gravitation are calculated according to Brockmann (1993). The losses caused by cyclone-ejector dilution unit system are determined experimentally by simultaneous measurements with a cyclone-ejector dilutor-BLPI system and a cyclone-BLPI system. The results are not necessarily applicable to ejector dilution in other combustion processes but to the recovery boiler.

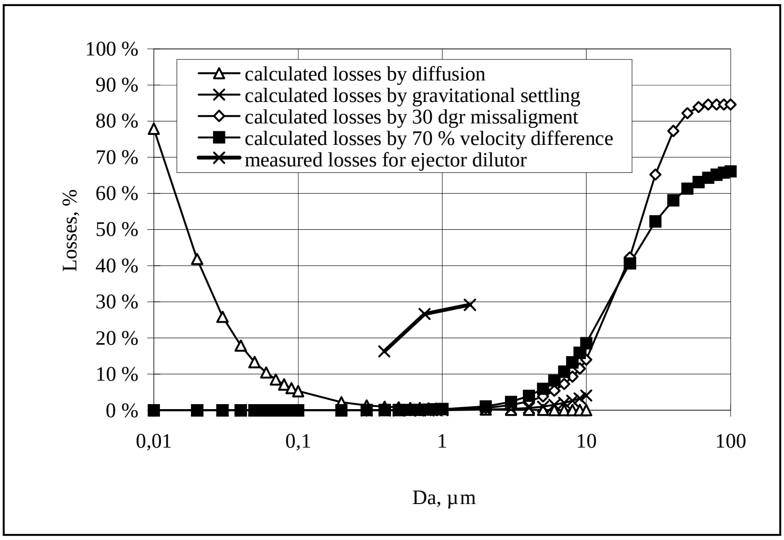

Figure 2. Estimated maximum sampling losses by diffusion and gravitation as well as in the probe inlet by isokinetic sampling and by probe misalignment. Measured measured maximum sampling losses in the ejector dilutor.

The diffusion losses are significant to particles smaller than 0.1 µm. However, very few particles are smaller than 0.1 µm in diameter thus the diffusion losses are negligible in the sampling lines. Simultaneously, the losses caused by the non-isokinetic sampling or misalignment of the sampling probe inlets are effective for particles larger than 10 µm. In the recovery boilers, these particles are more affected by sootblowing (Paper D).

The coarse particles were measured with a settling chamber at the boiler furnace and at the superheater area. Preliminary results from the boiler furnace indicated that some of the particles reacted with the stainless steel collection substrates and that carryover particles deposited in the device inlet (Mikkanen et al., 1998a). Thus a nitrogen flush was introduced. During the sampling at the superheater area, the chamber was flushed with a nitrogen flow and the samples were stored in a dry nitrogen atmosphere in order to avoid further reactions of the particles. However, the losses in the inlet of this device remained significant. As a consequence of these difficulties and the unsteady combustion in the recovery boiler, the coarse particle concentration and composition results are semiquantitative.

4.2 Chemical analyses and electron microscopy

The size classified BLPI samples, the bulk ash samples from the total particle concentration measurements as well as from the dust hoppers and the electrostatic precipitator catch were analysed for water soluble Na, K, SO_4, Cl, Ca, Mg, NH_4, NO_3 and, in some cases, for CO_3-ions with ion chromatography (IC). The size classified BLPI samples were analysed for Al, Fe, Si, Mn, Mg, and Rb with inductively coupled plasma mass spectrometry (ICP-MS).

Crystalline species in the bulk ash samples and in individual BLPI size classes were analysed using X-ray diffraction (XRD; Cahn et al., 1992). The diffraction patterns were analysed for Na_2SO_4, $K_3Na(SO_4)_2$, NaCl, Na_2CO_3, K_2SO_4, $KHCO_3$ and $CaCO_3$ crystalline phases. Furthermore, the forms of occurrence of sulphur, chlorine, and potassium were analysed with X-ray absorption fine structure (XAFS; Shah et al., 1995). The XAFS method provides direct data on the major compounds of a particular element in a sample, both in amorphous and crystalline form.

The particle composition, morphology and size were studied with electron microscopy. Scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectroscopy analyser (EDX) was utilised in several ways (Papers C–G). Individual particles were studied for morphology and size with low acceleration voltages (1–2 kV; Joy, 1985). The same individual particles were analysed with EDX using high voltages (8–10 kV; Goldstein et al., 1992) for elemental composition. Furthermore, coarse particle and deposit sample cross sections were studied with back scattered mode (BSE; Goldstein et al., 1992). Computer controlled scanning electron microscope (CCSEM; Shah et al., 1995) studies were applied for coarse particles. During the CCSEM analyses the system automatically rasters the electron beam across the filter and detects 1200 particles. The size of the particles is recorded along with the analyses data determined with EDX. A transmission electron microscope (TEM; Williams and Carter, 1996) was used for determining the crystallinity of individual particles. Since alkali salt samples are not stable under the electron beam, only very low illuminations were used.

4.3 Recovery boiler simulation

A combustion aerosol model called ABC (Jokiniemi et al., 1994) that includes mechanistic fume particle formation and growth, as well as deposition models, was utilised during this study. In the ABC model, gaseous species balance equation and the general dynamic equation of aerosols are solved simultaneously as a function of a time-temperature history a flue gas parcel experiences as it goes through the furnace and the flue gas channel (Jokiniemi et al., 1994, Paper B). It is assumed that the flow is turbulent and that aerosol and vapour compositions are uniform over the cross section of the flue gas channel. In addition, in deposition calculations both laminar and turbulent boundary layers can be considered. The calculation step length is determined by characteristic time for nucleation, coagulation, condensation and deposition. Consequently, the aerosol number and mass size distributions, composition size distribution, deposition and gaseous species concentration and composition are solved in an adaptive number of locations along the flue gas channel.

Because of the plug flow method applied in ABC, the recovery boiler simulations are carried out for the main flow, only. The elemental flow rates for C, Cl, S, H, O, N, Na and K were calculated from the mass balance of the recovery boilers (Papers D–F). The total particle concentrations, compositions, and the flue gas compositions were measured during the experiments at the boiler exit. However, the flue gas flow rate is seldom measured at the recovery boilers. Thus the flue gas flow rate was calculated based on the water content in the black liquor and in the flue gas, or based on the nitrogen concentration in the combustion air and in the flue gas. To minimise the effect of uneven flow across the furnace and flue gas channel, estimated effective cross sections were applied. The value for the recovery boiler furnace was 70% and for the convective section 80% of the boiler construction values.

The calculation starts in the hottest part of the boiler furnace where all the species except the seed particles and the inert coarse particles were assumed to be in the vapour phase. The seed particles were assumed 30–40 nm in diameter and 0.2% of the total particle mass concentration. The coarse particles were introduced as inert spherical particles with an average number diameter of 40 µm and concentration of 20% of the total particle concentration (Paper E). The input particle characteristics were estimated from the experimental data and from the sensitivity analyses (Paper B; Jokiniemi et al., 1995; Eskola, 1997).

Since the knowledge on detailed conditions in the recovery boiler furnace is limited, the model sensitivity for initial furnace temperature gradients, for the presence of seed particles and for a delayed sulphation of hydroxides was studied by Jokiniemi et al. (1995) and by Eskola (1997). For typical temperature gradients in the recovery boilers, the calculated fume particle size distribution agreed with the measured one. Similarly, the calculated mean particle size agreed with the measured one while the seed particles were present as inert particles from the beginning of the simulation. In a case, were the seed particles were absent, the mean particle size was significantly larger than the measured one. In some calculations, the sodium sulphates were not allowed to form in order to study the effect of slow sulphation of hydroxides or carbonates. These reactions had no effect on the particle size distribution, only on the particle composition.

The fume formation chemistry in the recovery boiler is described with the following global reactions (Paper B). Gas phase species distribution is calculated assuming ideal equilibrium locally. At high temperatures, the volatilised Na and K converts rapidly to hydroxides and chlorides. As the temperature decreases, these compounds convert to sulphates by reaction with SO_2 (equations 8 and 10). When there is not enough SO_2 to bind all Na and K, these species convert to carbonates by surface reaction (equation 9). Sulphation of carbonates can occur due to e.g. poor mixing in the furnace (equation 11). The following reactions apply to potassium, as well.

$T_g > 1300°C$ (fume particle formation):

$$2NaOH(g,c) + SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrow Na_2SO_4(g,c) + H_2O(g) \tag{8}$$

$1000°C < T_g < 1300°C$ (fume growth)

$$2NaOH(g,c) + CO_2(g) \leftrightarrow Na_2CO_3(c) + H_2O(g) \tag{9}$$

800°C < T_g < 1300°C (fume growth)

$$2NaCl(g,c) + SO_2(g) + \frac{1}{2}O_2(g) + H_2O(g) \leftrightarrow$$

$$\leftrightarrow Na_2SO_4(g,c) + 2HCl(g) \qquad (10)$$

$$Na_2CO_3(c) + SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrow Na_2SO_4(c) + CO_2(g) \qquad (11)$$

The coarse particle characteristics are introduced in the code as input. These particles deposit efficiently in the superheater area and consequently they are not predicted to exist at the boiler exit. However, the experimental results show a clear coarse particle mode, which forms by re-entrainment of particles from the heat exchangers, which, in turn, was not included in the calculation.

The calculated and the simulated fine particle size distributions and flue gas compositions agree very well. However, the simulated size distributions are narrower than the measured ones. This is at least partly due to the incomplete mixing in the actual recovery boiler, which causes some of the particles measured at one location to experience different time-temperature histories from the others, whereas all simulated particles at one location have the same time-temperature history. In the recovery boilers, simulation of the particle formation by gas-to-particle conversion is applicable since the concentration of vapour species is very high and since the number of compounds is reasonable. However, in coal combustion particle formation simulations the contribution of fume particles is less significant and vast experimental data for mineral transformations is reguired.

5. Results and discussion

In this thesis, the results of the extensive particle characterisation experiments carried out on five operating recovery boilers are summarised. Mass balances of the recovery boilers, enrichment factors, particle concentrations and compositions are presented. However, in order to investigate the particle formation mechanisms more detailed information is needed. The particle size distribution results along with the data on particle morphology are discussed and compared with the simulation results.

5.1 Extent of release and enrichment in particles

Even though the knowledge of the location of the release of inorganic species is limited, the overall extent of release and enrichment factors (Equation 1) can be estimated from the mass balance. These results, based on 100 kg of dry solids of black liquor, are shown in Figure 8 of Paper D, in Figure 4 of Paper E, and in Figure 3 of Paper F. The extent of release of Na was 10–12 % at the boiler exit, which was higher than earlier reported values (Borg et al., 1974; Warnqvist, 1973). Simultaneously, the extent of sulphur release has remained almost constant. Since the boiler heat loads, i.e. steam flow divided by the boiler hearth area, have increased over the years, it is evident that the furnace temperatures have increased, which in turn causes increasing sodium release. Since the sulphur release has not increased correspondingly, our results indicate that sulphur release is less sensitive to the furnace temperature than sodium release. The increase in Na release while S release remains almost constant is observed in the enrichment factors, as well. The enrichment of Na/S increases with increasing heat load (Figure 9 of Paper D). However, the enrichment factor of K/Na is independent of the boiler heat load. This indicates similar release mechanism for Na and K in boilers firing low Cl black liquor.

5.2 Particle concentrations and compositions

The total particle concentrations in the measured recovery boilers varied from 14 to 32 g/Nm^3. These values were mainly influenced by sootblowing, which is continuously operating along the flue gas channel. During sootblowing, the deposit layer is removed from the heat exchangers with a steam jet. Some of the re-entrained particles follow the gas flow and thus momentarily, the total particle concentrations exceeded 30 g/Nm^3, while the fume particle concentration remained constant at about 10 g/Nm^3 (Paper D). The fume and coarse particle concentrations measured at the superheater area and the boiler exit of the UPM-Kymmene Wisaforest mills recovery boiler are shown in Table 2 (Table 6 of Paper D and in Table 5 of Paper F), and the compositions in Table 6 of Paper F.

Table 2. Sample of particle size fraction mass concentrations as measured at superheater area and boiler exit of the UPM-Kymmene Wisaforest mills recovery boiler. Measurement results reduced to dry flue gases with 3 v-% of O_2.

	Particle size fraction	**Unit**	**Particle concentration or particle fraction**
Total particle concentration at superheater area		g/Nm^3	26
Fine particle fraction at superheater area	< 3 µm	%	56
Intermediate particle fraction at superheater area	3–20 µm	%	1
Coarse particle fraction at superheater area	> 20 µm	%	43
Total particle concentration at boiler exit		g/Nm^3	17
Fine particle fraction at boiler exit	< 3 µm	%	66
Coarse particle fraction at boiler exit	> 3 µm	%	34

The fume particle concentration measured at the boiler exit increased from 11 g/Nm^3 to 14 g/Nm^3 as the heat load increased from 0.5 kg/s/m^2 to 0.7 kg/s/m^2 (Paper D) because of enhanced release of sodium and potassium. In addition, the fume particle concentration was lower during combustion of the black liquor originating in hardwood or mixedwood pulping as compared to the black liquor originating in softwood pulping. However, the fume particle concentration showed no rapid changes, as discussed later.

At the superheater area, the coarse particle concentration was more than 40 % of the total particle concentration, which is a significantly higher value than what has been reported earlier (e.g. Siiskonen and Mäntyniemi, 1994; Backman et al., 1995). However, the earlier results are based on the deposition probe measurements, where the deposit sample removed from the windward side was assumed to consist of coarse particles and from the leeward side of the fume particles. This approach may cause an error since the windward side of the deposit consists of a mixture of both the fume and the coarse particles (Gökoglu and Rosner, 1983). Furthermore, the deposit layer may erode during collection of the deposit sample thus decreasing the estimated value for the coarse particle concentrations (Paper G), as discussed later.

The average fume particle compositions as Na:K:S:Cl molar ratios measured at the superheater area were 1:0.06:0.43:0.04 (Paper F) and at the boiler exit 1:0.08:0.45:0.04 (Papers D and F) during our experiments. These molar ratios are in agreement with earlier measurement (Esplin et al., 1973). In addition, the molar ratio results are in good agreement with the XRD and XAFS results, suggesting presence of Na_2SO_4 as the main component and minor fractions of $K_3Na(SO_4)_2$, and NaCl. The lowest molar ratio of Na/S occurred in a situation when the furnace heat load was at its lowest and consequently the sodium release was low. The low sodium concentration combined with insufficient mixing in the flue gas caused poor sulphur capture and thus the SO_2 value in the flue gases was higher than 1000 ppm.

During our experiments, the coarse particle composition measured at the superheater area as Na:K:S:Cl molar ratios were 1:0.07:0.46:0 and during sootblowing 1:0.07:0.40:0.03, and at the boiler exit 1:0.06:0.43:0.04 (Paper F). The coarse particle composition results are in agreement with the XAFS and CCSEM results indicating that the coarse particles at the boiler exit are mainly sodium sulphate along with a minor concentration of a $K_3Na(SO_4)_2$ and NaCl (Paper D). Furthermore, the EDX results indicate presence of calcium, silicate and magnesium rich particles in minor amounts (Papers C and F). The molar ratio results are in good agreement with the earlier reported values 1:0.08:0.44:0.19 for a 'hot' furnace (Hupa et al., 1998) and 1:0.05:0.46:0.12 (Tran, 1986), except for Cl. The discrepancy in the Cl concentration is most likely a consequence of the measurement method. The previously presented values include the Cl rich fume particle fraction depositing on the windward side of the deposition probe, as discussed earlier. In addition, these samples may contain the deposited Cl vapours. Moreover, our measurements were carried out between the superheaters where the largest particles have deposited prior to the sampling site. Since the largest particles are black liquor droplet residues, they are likely to contain Cl, which was detected in the deposition probe measurements.

5.3 Particle mass, composition and molar ratio size distributions

The mass size distribution of the recovery boiler fly ash was found to be bimodal at the boiler exit and trimodal in the superheater area (Papers A and F). Based on this result the fly ash particles smaller than 5 µm in aerodynamic diameter are called fume particles in this thesis, the particles in the size range 5–500 µm are called coarse particles and the particles larger than 500 µm in aerodynamic diameter are called carryover particles. The mass size distribution of the fume particles at the boiler exit, as well as the coarse particles at the superheater area and at boiler exit are shown in Figure 3, as determined with the BLPI and double cyclone system at UPM-Kymmene Wisaforest mills recovery boiler.

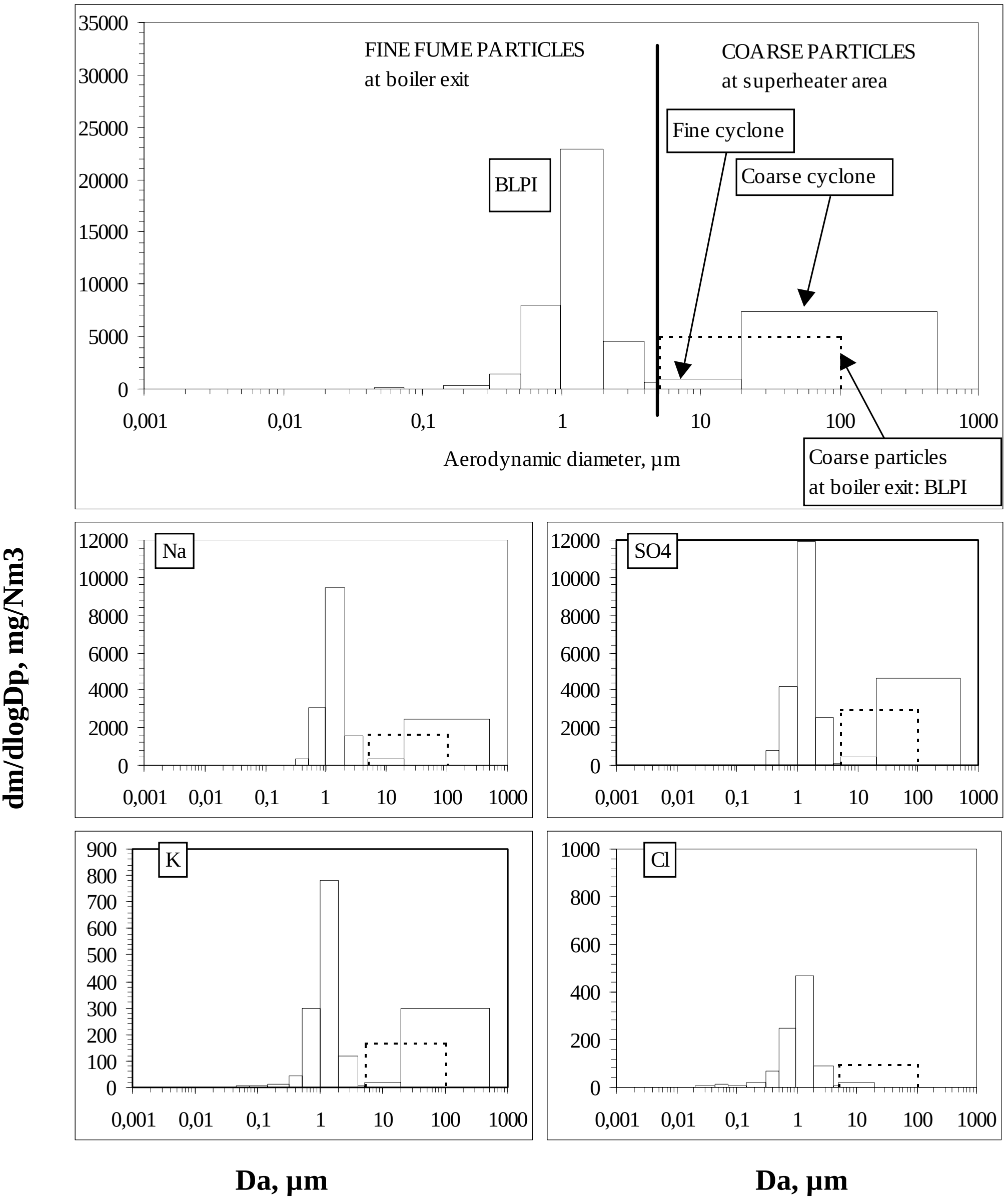

Figure 3. Mass and composition size distributions as measured at superheater area with double cyclone and at boiler exit with low pressure impactor (BLPI) and analysed with ion chromatography for water soluble Na, K, SO_4 and Cl – ions. The measurements were carried out at UPM-Kymmene Wisaforest mills recovery boilers.

The composition size distributions were obtained by analysing each of the particle size fractions for the main ions Na, K, SO_4 and Cl or for the refractory metals Al, Fe, Mg, Mn, Si and Rb (Paper D). Subsequently, molar ratios were calculated for Na/SO_4, K/Na and Cl/K (Papers A, D and E). The mass and composition size distributions presented in Figure 3 are a typical example of particle characteristics measured in the recovery boilers. Corresponding size distributions for the fume particles are shown in Paper D and for the coarse particles the results are shown in Paper F.

5.4 Fume particles

The mass size distribution of the fume particles expressed as aerodynamic diameter peaks at about 1.1 µm at the furnace exit and at almost 2 µm at the boiler exit. At the furnace sampling site, alkali chlorides are still partly in the vapour phase prior to sampling. However, the vapour concentration is not high enough to result in the growth of the major particle mode from 1.1 µm to 2 µm nor to nucleate and form new particles. Thus the particles grow by another mechanism, most likely agglomeration (Paper B).

The number concentration of fume particles measured at the furnace exit was about $2 \cdot 10^8$ #/Nm^3. The particles in such high number concentrations continue to collide. This causes the number concentration to decrease and particle size to increase from the furnace exit to the boiler exit (Paper B, Figure 8 of Paper E), as shown in the measured and calculated number size distribution in Figure 4a. The mean average particle mobility diameter at the furnace exit was about 0.3 µm and at the boiler exit about 0.4 µm. The measured and the calculated results are in good agreement, as shown in Figure 4a.

The size of the fume particles was not affected by the boiler operation, even though the concentration increased while the boiler heat load increased, as discussed earlier. Moreover, the fume particle size or concentration showed no rapid changes. As an example, the effect of sootblowing studied at UPM-Kymmene Kuusankoski mills recovery boiler is shown in Figure 4b. No change in the fume particle size distribution was observed during sootblowing. At the same time, the influence of the preimpactor of the DMA/CNC system was observed to be significant (Figure 4b). This partly explains the discrepancy in the measured and the simulated size distribution results discussed later.

The shape and size of individual fume particles was analysed with SEM. The individual fume particles collected at the furnace were rather spherical and about 0.1–0.4 µm in diameter. At the boiler exit, the fume particles were agglomerates formed from a few primary particles of 0.3–0.7 µm in diameter. The primary particles have grown to the final size by coalescence, heterogeneous condensation and chemical reactions (Paper B). Agglomerates with less than twenty primary particles are formed in the flue gases. At temperatures lower than the melting point of sodium sulphate-potassium sulphate mixture (about 850°C), the particle coalescence is not complete and agglomerates are formed. A representative agglomerated structure of the fume particles present in the measured recovery boilers is shown in Figure 5.

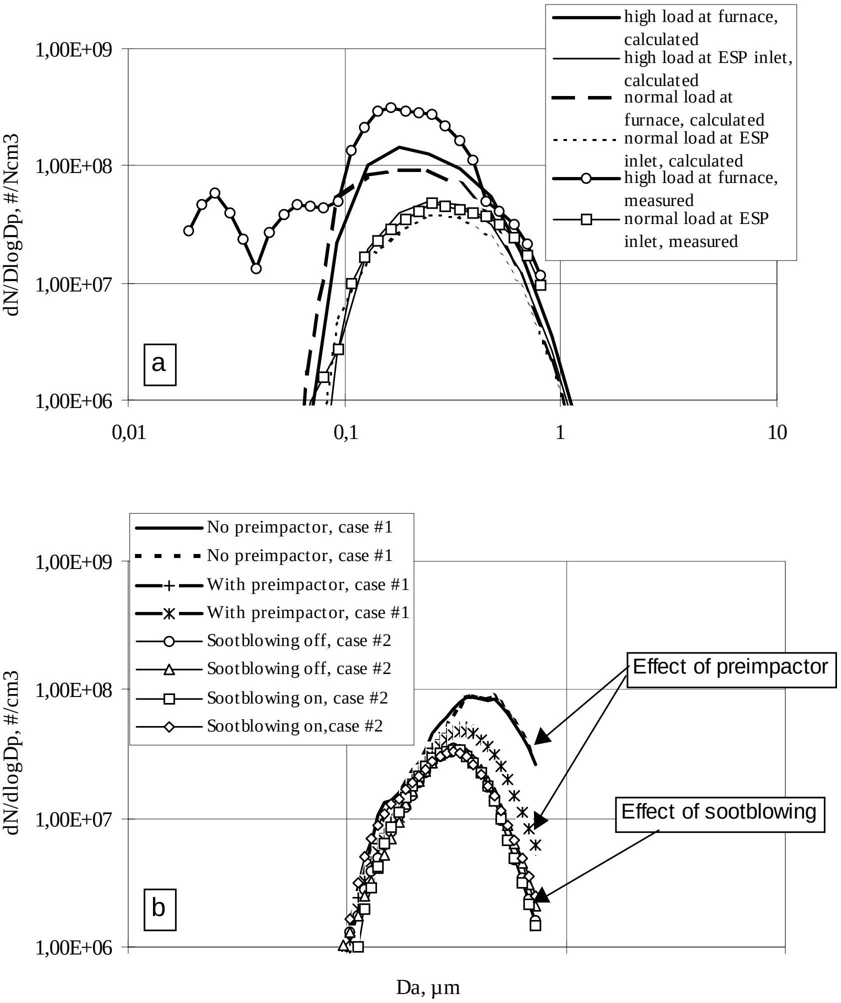

Figure 4. Number size distributions measured with DMA/CNC: a) the measured number size distribution at the recovery boiler furnace and at the boiler exit on UPM-Kymmene Kaukas mills recovery boiler and corresponding size distribution calculated with the ABC code and b) showing the effect of preimpactor on the mean average size and the stability of distribution during sootblowing at the UPM-Kymmene Kuusankoski mills recovery boiler.

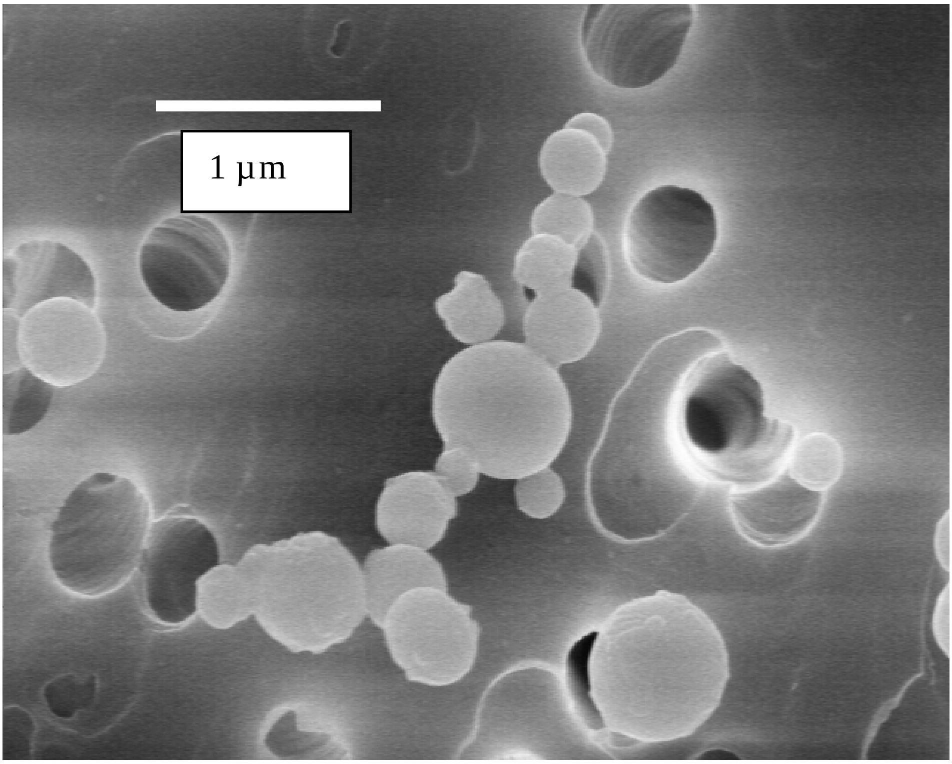

Figure 5. Fine fume particles collected on planar filter at boiler exit of UPM-Kymmene Kuusankoski mills recovery boiler. The small agglomerated structure and the individual fine particles are seen.

The measured and the calculated particle size distributions have a discrepancy (Paper B, Figure 9 of Paper E). This is due to the particle morphology, which is spherical in the ABC model even though a significant fraction of fume particles has agglomerated open structure that enhances agglomeration as compared to the spherical particles of the same mass. Nevertheless, the difference in the measured and calculated size distributions is not discouraging considering the simplifications involved in the model.

The composition size distributions for Na, K, and SO_4 are similar to the mass size distributions. The operation of the boiler has a minor effect on the shape of the size distribution of these elements, yet the concentrations of the particles vary. The molar ratio of Na/SO_4 of 2 indicates that the particles contain mainly Na_2SO_4. This is consistent with the XRD and XAFS results showing that the main component in the particles is Na_2SO_4. The high value of Na/SO_4 (about 3) in the furnace during high load operation indicates that mixing or residence time is not sufficient for Na_2SO_4 to form. The corresponding molar ratio in boiler exit is 2.1 (Paper D). Since SO_2 levels were very low during the experiments and since the sulphation of NaOH is rapid enough to form Na_2SO_4 in furnace conditions (Mikkanen et al., 1999), thus the results indicate presence of Na_2CO_3 in the fume particles at furnace. The composition size distributions of Na, K and SO_4 are in good agreement with the calculated results, as well (Paper E).

In the size distributions measured at the furnace of UPM-Kymmene Kaukas recovery boiler, Cl was obsered to be enriched in particles smaller than 0.1 µm. This indicates that a fraction of alkali chlorides has been in the vapour phase prior to sampling. The Cl size distributions measured at the boiler exit are similar to the overall mass size distributions, even though a slight broadening of the main mode to the smaller particles can be detected. If Cl condensed heterogeneously on individual particles prior to agglomeration, the composition size distributions would practically be similar to the mass size distributions, as observed in the simulation results assuming spherical particles (Paper B). However, since the agglomerated particles sinter somewhat, broadening of the Cl size distribution indicates that primary particles have agglomerated and partly sintered prior to the condensation of chlorides. Subsequently, the chlorides may mix with the pre-existing salts or form a layer on the agglomerate surface. In both of these cases, the sintering of the particles would be enhanced (e.g. Kingery, 1976).

The composition size distributions of refractory metals are shown in Figure 12 of Paper D. Rb composition size distribution is similar to the total mass size distribution indicating that as an alkali species Rb behaves similarly to Na and K. The elements Al and Mg are only present in the coarse particles indicating that they are not evaporating during the process. The composition size distributions of Fe and Mn are clearly bimodal indicating that a fraction of these elements has volatilised. Since the equilibrium vapour pressures of the oxides of these elements are very low, they are likely to form seed particles in the combustion boundary layer. The presence of seed particles was indicated by the sensitivity studies for the fume formation, as well (Paper B; Jokiniemi et al., 1995).

The individual fume particles collected from the furnace during high heat load operations show almost completely coalesced morphologies whereas the particles collected during low heat load operation have only partially coalesced (Figure 13a,b of Paper D). During high heat load operation furnace temperatures are higher and the residence times are shorter than during low heat load operation. Likewise, particles collected at boiler exit during high heat load operations show more coalesced morphologies, in this case thicker necks, between the agglomerated primary particles than during low heat load operation (Figure 13c,d of Paper D). However, the analysis results suggest that there are less double salt particles present and Cl concentration is ten times lower during the high heat load operation than during the low heat load operation. Both of these results indicate a higher melting temperature of the particles during the high heat load operation. This indicates that the thicker necks have formed prior to the chlorine condensation on the particles, thus suggesting that the higher furnace temperature has resulted in more complete coalescence. Even though the sintering of the small agglomerates might not affect the deposition of the particles, it might have an impact on the deposit layer characteristics or on the gas cleaning efficiency.

5.5 Coarse particles

Six coarse particle types were categorised according to their appearance and composition: i) swollen black liquor droplets that were larger than 500 µm in diameter, ii) spherical particles 5–100 µm in diameter which appeared highly porous inside, iii) dense spherical particles about 2–250 µm in diameter, iv) irregular, rough particles 3–40 µm in diameter, v) agglomerates that consisted of hundreds of primary particles of 0.3–0.7 µm in diameter, and vi) sintered irregular particles 30–250 µm in diameter (Paper F; Mikkanen et al., 1998a).

5.5.1 Coarse particles generated in the furnace

Four types of coarse particles are entrained from the furnace. The largest ones (i) that are seldom detected at the furnace exit of a modern boiler are the unburned black liquor droplets, i.e. carryovers. The other types can be related to the extent of burning process of the black liquor droplets. As a consequence, the particle size of these particles varied from 2–250 µm.

The spherical particles appearing highly porous inside (ii) are likely residues of burning carryover particles. The outer surface of these particles is solid, which indicates melting, and the inner structure indicates vaporisation and partial sintering. Furthermore, the EDX analyses on these particles suggest enrichment of potassium and a high Na/S ratio, which suggests presence of K_2CO_3 and Na_2CO_3 Since the decomposition temperature is higher for K_2CO_3 than for Na_2CO_3, and since the suggested release mechanism for fraction of potassium is decomposition of carbonate (Wåg et al., 1997), this result indicates that the origin is in black liquor droplet. These particles are seldom detected in the boiler exit. There are, however, earlier observations of this kind of particles in recovery boilers (Nguyem and Rowbottom, 1979) and in laboratory experiments (Reis et al., 1995; Mikkanen et al., 1998b).

The solid spheres (iii) are sintered residues of black liquor droplets or these could originate in mechanically released salt residues (Verrill et al., 1994; Kohesfahani et al., 1998; Mikkanen et al., 1998b), as well. The EDX analysis results indicate that these particles are salt residues rather than sintered agglomerates or carryover residues. The study on cross sections of these particles indicates that they have been completely molten (Figure 6). These particles deposit efficiently on the heat exchanger and thus only the smallest ones are detected at the boiler exit.

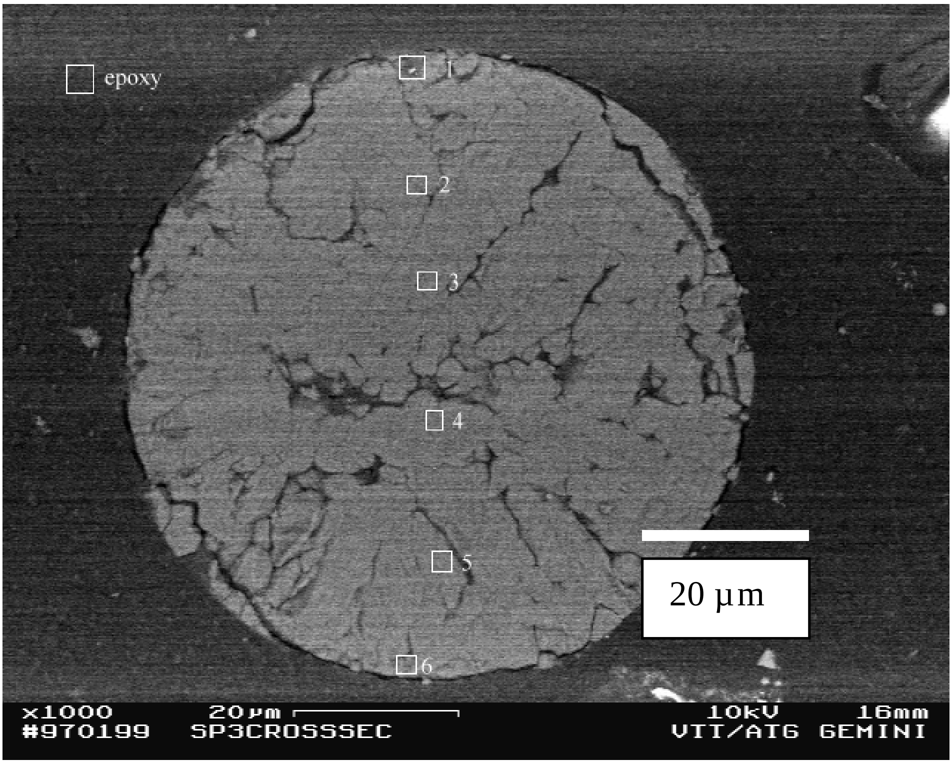

Figure 6. Cross section of a coarse smelt residue particles collected with settling probe at superheater area of UPM-Kymmene Wisaforest mills recovery boiler. These particles form from ejected black liquor droplet fragments or from smelt bed surface as molten salt beads.

The irregular, rough particles (iv) show Si, Ca and even traces of Mg in the EDX spectra. At the boiler exit, these particles are often spheres of about 1–20 µm in diameter. These particles are so large that they could not have formed from vapours. The composition and the shape of these particles indicate that they form from impurities in the black liquor.

5.5.2 Re-entrained particles

The large agglomerates (v) are formed from the fume particles and are detected at the boiler exit. The primary particles are about 0.3–0.7 µm in diameter as in the fume agglomerates, but the degree of coalescence is higher for the large agglomerates than for the fume agglomerates. The residence time in the recovery boilers is less than 20 s, which is too short for this size of agglomerates to form via Brownian motion thus they form by some other mechanism than collisions in the gas phase most likely by re-entrainment of deposits from the heat exchanger surfaces (Paper D). In fact, since the majority of the coarse particles in the boiler exit originate in the fume particles which have been re-entrained from the heat exchangers, the results suggest that a significant fraction of the deposited fume particles are re-entraining back into the flue gas flow (Papers F and G).

The re-entrainment of fractions of the deposited layer was evident in the deposit layer growth study reported in Paper G. The deposit growth rates did not correspond to the main deposition mechanisms but it was obvious that some other mechanism, most likely erosion of the layer, was governing the deposition growth rate especially for porous deposit layers. The erosion or re-entrainment of particles can occur spontaneously in unstable flows like in the recovery boilers as agglomerates (Matsusaka and Masuda, 1996). Furthermore, a TEM study on the fume and coarse agglomerated particles collected in the gas phase and on a fraction of the deposit layer shows that all the particles are crystalline. However, the crystallinity of the coarse agglomerated particles and the deposit layer is similar, while it is different for the fume particles (Mikkanen et al., 2000). This further confirms that the origin of the coarse agglomerated particles is in the deposit layer.

The sintered irregular particles (vi) form by deposition and subsequent sintering of the fly ash particles on the heat exchangers. Particles like this are detached from the heat exchangers during sootblowing and due to their large size they are re-depositing prior to the boiler exit.

As discussed earlier, the coarse particles are depleted in Cl at the superheater area. On the other hand, Cl is detected in the sintered irregular coarse particles and the highest Na/S molar ratios are measured in the coarse particle fraction in the superheater area while the sootblowing is operated. These results suggest, that the particles re-entrained from the heat exchangers by sootblowing may not have reacted with SO_2 in the flue gas to release HCl, whereas the particles re-entrained from the heat exchangers without sootblowing have residence times long enough or temperatures high enough to react with SO_2. On the other hand, Cl may penetrate the deposit surface as vapour and deposit in the cooler part of the layer, which is then removed by sootblowing. Both these explanations suggest that the coarse particles at the boiler exit containing Cl have formed in the flue gas channel sections where the flue gas temperature is too low for significant sulphation to occur during a sootblowing cycle or the Cl vapour phase concentration is minimal.

The results on coarse particles are only semiquantitative, even though the coarse particle categories were clearly distinguished from each other. With the knowledge of the black liquor combustion process and of the deposition and re-entrainment, the coarse particle formation mechanisms are proposed. However, since the experimental data on the coarse particles in the gas phase in operating recovery boilers is very limited, no attempt to model their formation has been taken.

6. Conclusions

The formation mechanisms of fume particles and coarse particles in recovery boilers were determined based on experimental and modelling studies. Particle measurements were carried out in the furnace exit at about 900°C, in the superheater area at about 750°C, and at the boiler exit at about 150°C in order to study gas-to-particle conversion and particle growth, as well as coarse particle characteristics in industrial scale recovery boilers. Unlike in the earlier studies, the measurement setups were designed for extracting the samples directly from the flue gas to avoid uncontrolled transformations of samples during measurements. With these novel measurement methods the total particle concentration and compositions were detected and individual particles were collected for characterisation. For the first time, the fume and coarse particles of recovery boilers were characterised to such a detail. The results of this thesis can be utilised in the design of the heat exchangers and placement of sootblowers due to more accurate prediction of fly ash particle deposition. Furthermore, the flue gas-cleaning devices can be optimised according to the detailed fly ash particle characteristics.

Figure 7 summarises the main formation and growth mechanisms of fume particles in recovery boilers. The results indicate that particle formation initiates seed particles are formed in the boundary layer of a burning black liquor droplet or char bed. It is assumed that the sodium is released as NaOH or Na_2CO_3 from the combustion boundary layer, but that most of the Na_2CO_3 is decomposed in the hot zone of the furnace. The particles grow because NaOH reacts with SO_2 to form Na_2SO_4, which rapidly condenses on existing seed particles or nucleates, or because Na_2SO_4 forms on surfaces of existing particles. The particles are simultaneously growing by coagulation, which decreases the number concentration, and in turn decreases the collision frequency of the particles. At some temperature, the coalescence becomes slower than the particle collisions, hence agglomerates are formed. Increasing particle viscosity due to decreasing flue gas temperature retards the coalescence and thus the formed agglomerated particles continue to deform by sintering. The degree of sintering of the fume agglomerates is mainly influenced by the furnace temperature. The chlorides condense after the agglomeration of the fume particles.

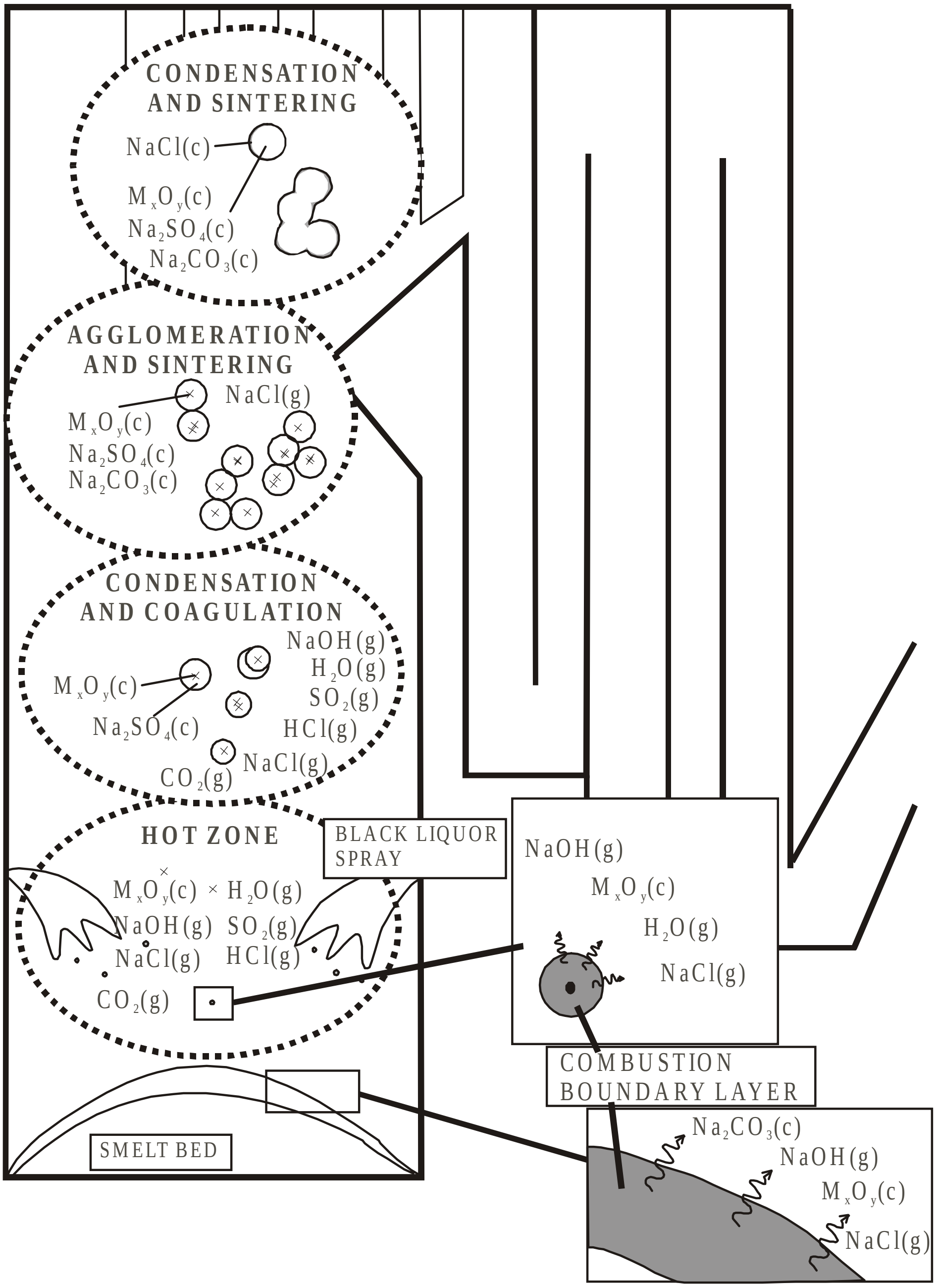

Figure 7. Schematic of fine fume particles formation in recovery boilers.

The figure presents sodium as the only active alkaline, although the same mechanisms apply to potassium, too. Moreover, even though the locations of the main mechanisms are presented in the schematic, only the assumption that the particles form inside the furnace and not in the superheater area was confirmed.

The coarse particle formation mechanisms are shown in Figure 8. The particles exiting the furnace originate in the burning black liquor droplets or from the char bed. The largest particles are partly volatilised swollen black liquor droplets, larger than 500 µm in size. In modern boilers, this kind of particles are seldom detected in the superheater area. The spherical particles that are highly porous inside form from droplet residues that volatilise more than the large droplet residues. The size of these particles is 5–100 µm in diameter and they are enriched in potassium. Dense spherical particles are 2–250 µm in diameter. The composition and the cross sectional structure of these particles suggest that they form as ejected smelt residues that are entrained from the furnace. Most of the coarse particles carried over from the furnace are smelt residue particles. However, since they efficiently deposit in the superheater area, only the smallest ones are detected in the boiler exit. The composition of these three types of particles presented above can be related to a progressive degree of vaporisation and char burning of black liquor droplets. In addition, a particle type originating in mineral impurities in the black liquor is observed to exit the furnace.

In addition to the particle types exiting the furnace, large agglomerates which consist of hundreds of 0.3–0.7 µm diameter primary particles and sintered irregular particles 30–250 µm in diameter are observed. These coarse particles form when the fume particles deposit onto the heat exchangers, sinter and entrain into the flue gas. Entrainment of particles occurs due to sootblowing or spontaneously in the flue gas channel. The sintered irregular particles are the major mode of particles during sootblowing at the superheater area.

The mass concentrations of the particle modes varied along the flue gas channel and depending on the boiler operation. In general, the fume particles were the major mode, except during sootblowing, when fractions of deposit layer were entrained to the flue gas causing locally very high coarse particle concentrations. The coarse particle mass fraction was about 40% at the superheater area, where the coarse particle mode consisted of both burning black liquor or char bed originating particles and entrained deposit layer fractions. At the boiler exit, the coarse particle mass fraction was about 30 %. There the coarse particles were mainly entrained deposit layer fractions.

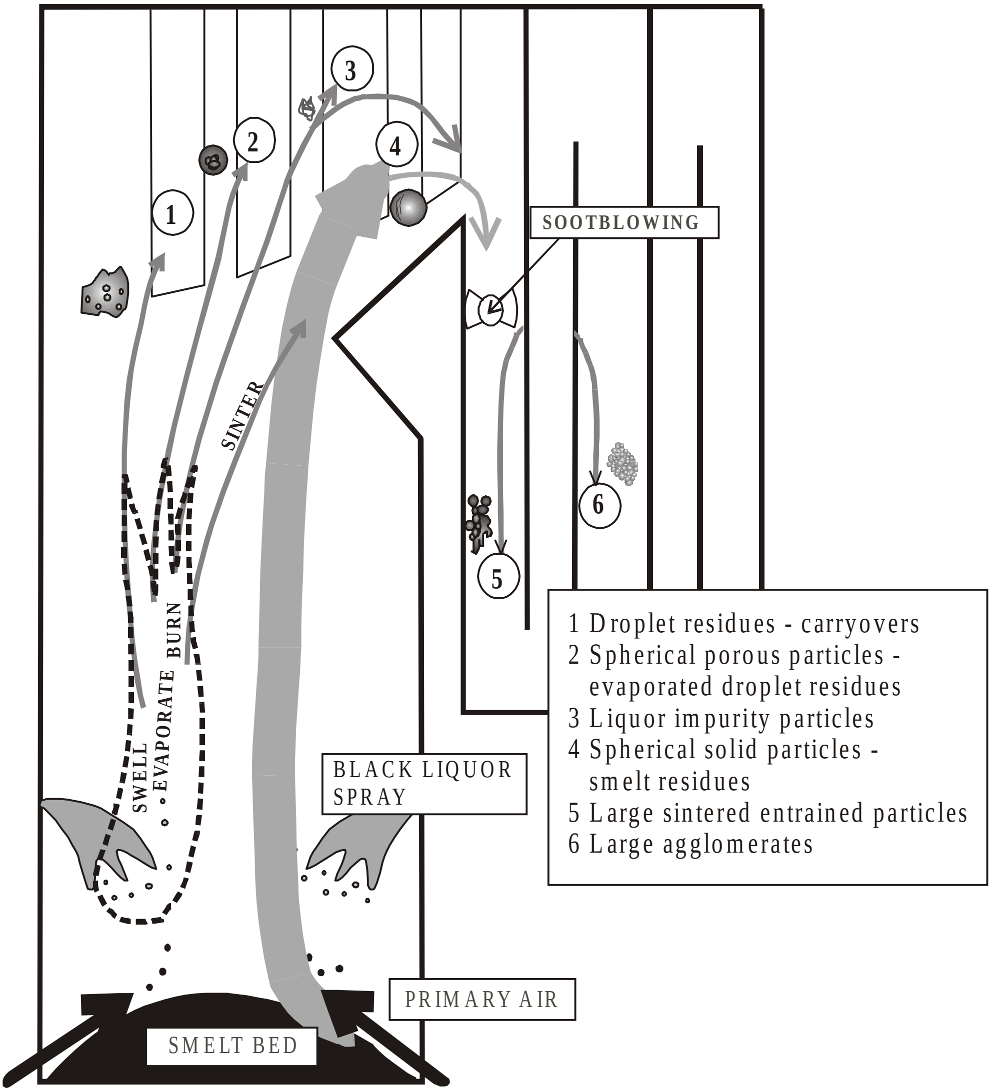

Figure 8. Schematic of coarse particles formation in recovery boilers.

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Fly ash particle formation in kraft recovery boilers

Abstract

Fly ash particle formation in the recovery boilers has been studied experimentally in five industrial scale recovery boilers operating in Finland. The formation and growth mechanisms of the particles were studied by measuring particle characteristics including number, mass and composition size distributions in the gas phase at the recovery furnace exit, at superheater area and at boiler exit. As part of the thesis work, measurement methods were developed for recovery boiler conditions. In addition to the experimental studies, the particle formation was simulated with an Aerosol Behaviour in Combustion (ABC) model, which includes models for gas-to-particle conversion and for deposition.

The results indicate that seed particle formation is involved in the fume particle formation. Particle growth occurs primarily in the furnace at temperatures greater than 800°C where the particles grow by simultaneous condensation and coagulation. Below the melting temperature of the particles, coalescence of the particles becomes slower than the particle collisions, due to increasing viscosity of the particles. Subsequently, the particles are not completely coalesced spheres but form agglomerated structures. The mean fume particle aerodynamic diameter measured at the furnace was 1.1 µm whereas it was almost 2 µm at the boiler exit. This growth is primarily due to agglomeration.

The results showed two sources of coarse particles. Coarse particles formed in the furnace were efficiently depositing on the heat exchangers. The other source, which turned out to be significant as well, is the re-entrainment of particle aggregates from the heat exchangers.

Keywords

fly ash, particles, formation, recovery boilers, black liquors, combustion, aerosols, nucleation, agglomeration, modelling

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