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# DEPOSIT PROBE MEASUREMENTS IN DANISH GRATE AND PULVERIZED FUEL BIOMASS POWER BOILERS.

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#### **ABSTRACT**

Several measuring campaigns with focus on deposition behavior have been conducted at full-scale power plants firing biomass in Denmark. These measuring campaigns have been reviewed in this work. The focus of the review is the obtained experiences on deposit formation, chemistry and shedding.

Corresponding samples of fuels, ash deposits and fly ash have provided information on the transformation of inorganics in the boiler. Generally, grate fired boilers provide a fly ash containing high contents of K, Cl and S compared to the fuel ash, while suspension fired boilers fly ash has a composition nearly similar to the fuel ash. Inner most biomass deposits are always salt-rich, while thicker deposit layers also contain some Si and Ca.

Deposit probe formation rate measurements have been performed in different ways on several boilers. Grate and suspension fired boilers seems to cause similar deposit formation rates. Suspension fired boilers generate more fly ash, while grate boilers form a fly ash with a higher fraction of melt formation (and thereby a higher sticking probability) at similar temperatures. For suspension fired units it is observed that wood with a lower ash content than straw gives rise to lower deposit formation rates.

The flue gas temperature is an important parameter in the deposit behavior of biomass-fired boilers. Increases in the flue gas temperature of both grate and suspension fired boilers leads to increased deposition rates and deposits with higher contents of Si and Ca. This can be explained by increased deposition by inertial impaction due to higher melt fractions of ash particles (containing Si and Ca) at increased temperatures.

The shedding behavior is influenced by exposure time, probe surface temperature, flue gas temperature and deposits chemistry. The influence of temperature on the degree of sintering varies with the fuel type. Possibly, increased contents of Si and Ca will lead to increases in the sintering temperature and thus to altered shedding behavior. It is recognized that the exposure time of the deposits in the flue gas influences the removability of the deposits.

Keywords: full-scale, grate, suspension, fly ash, deposits, shedding, chemistry, buildup rate

# 1 INTRODUCTION

As a consequence of Danish and international energy policy during the last 30-35 years, several full-scale measuring campaigns have been conducted in order to investigate the thermal conversion and utilization of straw for heat and power production - either in dedicated, grate-fired plants, in conjunction with coal in suspension boilers and lately also in dedicated biomass (wood and/or straw) fired suspension boilers.

Utilization of biomass for power production may increase the rate of formation of deposits, which are difficult to remove especially in the boiler chamber and on superheater coil surfaces compared to those formed during coal firing [1].

The difficulty arises from a high K-content of the biofuels, as potassium partly vaporizes and form chlorides and sulfates, which may condense on heat transfer surfaces. Potassium may also form low-melting Si-rich particles, which may stick to the heat transfer surfaces upon impaction [1]. Deposits are formed in biomass-fired boilers by at least four different mechanisms; Inertial impaction, thermophoresis, condensation and heterogeneous reaction [2]. The four mechanisms apply to different parts of the flue gas or fly ash. The large fly ash particles (>10 µm) are deposited by inertial impaction, when the particles have sufficient inertia to traverse the gas stream lines around a tube. Whether the particles then stick to the probe or are rebound, depends on the stickiness of the particle and deposit surface, thus on the melt fractions of these. Small aerosol particles (< 1 µm), often KCl or K<sub>2</sub>SO<sub>4</sub>, are deposited by thermophoresis, where a temperature gradient is the driving force for the transport of the particles through the gas phase toward the cold probe surface. KCl or K<sub>2</sub>SO<sub>4</sub> are also found as gaseous components in the flue gas. These may either condense or react heterogeneously on the deposit surface. The gas components are thus transported toward the surface by diffusion, with a concentration gradient being the driving force

Once formed, the deposits may be removed from heat transfer surfaces by shedding, either naturally or induced by e.g. soot-blowing. Various mechanisms of deposit shedding have been identified; erosion, gravity force (debonding/ melting) and thermal or mechanical stresses. The occurrence of shedding events depend on various physical parameters of the deposits; tensile and adhesive strengths, elastic properties, viscosity, melting behavior, thermal expansion coefficient and thermal properties. These physical properties leads back to the chemical composition and the temperature of the deposit, but are often complicated to describe [3].

In order to handle ash related boiler problems, careful design of boiler chambers, super heaters and soot-blowing equipment have been conducted. To support the development of biomass combustion equipment, deposit probe measurements have been performed in the last 20 years on many of the power plant boilers in Denmark. The measuring campaigns have been conducted in collaboration between power plant owners (now DONG Energy and Vattenfall) and Technical University of Denmark (DTU).

The focus of the present study is a review of the full-scale measuring campaigns, where biomass is fired without coal. The study includes a review of the applied experimental probe techniques, and an overview of data gained on deposit build-up rates, deposit removal, deposit chemistry and the influence of fuel type and boiler operation conditions on the processes.

## 2 EXPERIMENTAL

The experiments reviewed in this study have been conducted at several Danish CHP plants, both grate and suspension fired. The data for the plants are seen in Table 1. It should be noted that Avedøre unit 2 include two boilers; a straw fired grate boiler and a wood/oil/gas fired suspension boiler, which both provides steam for the steam turbine.

**Table 1**: Power plant data for the plants mentioned in this work

	Firing	Fuel	Thermal	Steam	Steam	Commercial	
	system		input	Temp	Pressure	operation	Ref.
			$MW_{th}$	°C	Bar		
Haslev	Cigar burner	Straw	23	450	67	1989	[4,5]
Slagelse	Grate	Straw	31	450	67	1990	[4,5]
Rudkøbing	Grate	Straw	10.7	450	60	1990	[4,6]
Masnedø	Grate	Straw	33	522	92	1996	[4,7]
Ensted	Grate	Straw	100	470	200	1998	[8]
Avedøre	Grate	Straw	100	545	310	2001	[9,8]
Avedøre	Suspension	Wood/oil/gas	800	560	300	2001	[8]
Amager 1	Suspension	Straw/wood	350	540	185	1971/2008	[10,11]
Amager 2	Suspension	Straw/wood	250	480	90-110	1972/2003	[9,11]
Jordbro	Suspension	Wood	80			1968	[12]

In the investigated grate fired units, straw is the primary fuel. The straw is fed to the boiler on a grate on which the combustion takes place. Primary combustion air passes through the grate, and the temperature in the fuel-bed on the grate is typically in the range 1000-1200 °C [13]. From the grate, the majority of the ash is dumped into the ash pit at the end of the grate, while only a small fraction (typically less than 20 wt%) is entrained with the flue gas [14]. One of the CHP-plants included in this study, is 'cigar-fired', which implies that whole straw bales are introduced to the furnace and burn along the surface of the bale, where primary air is introduced by a jet, thereby stabilizing the combustion on the surface [5]. Table 2 lists the ash and deposit related measuring campaigns conducted in grate boilers and the type of examinations performed.

**Table 2:** Overview of the full-scale grate experiments performed in Denmark.

				<u>.</u>	Method		Examinations				
Ref.	Year	Boiler	Place	Fuel	Probe measurements	Mature deposit samples	Buildup-rate	Chemistry of deposits	Corrosion	Shedding	
[5]	1997	Haslev (cigar)	F, SH	Straw	X		X	X			
		Slagelse	F, SH	Straw	X		X	X			
[6]	1998	Rudkøbing	F	Straw	X			X	X		
[7]	2000	Masnedø	SH	Straw	X	X		X			
[15]	2004	Ensted	SH	Straw		X		X			
		Masnedø	SH	Straw		X					
[16]	2004	Avedøre 2	CP	Straw	X		X	X		X	
[17]	2006	Avedøre 2	F/SH,CP	Straw	X		X	X			
		Ensted	F	Straw	X						
[18]	2006	Avedøre 2	F/SH	Straw	X		X			X	

Places: F = Furnace, SH = Near super heaters, CP = Convective Pass

For grate-fired boilers, the investigations include both analyses of deposits collected on probes and of mature deposits collected from superheater tubes in the plant. The data set includes quantification of the rate of deposit formation, chemical analyses of fuels, ash and deposits, and in a few cases corrosion studies and shedding observations.

In biomass suspension-fired units, both wood and straw pellets have been utilized as fuels. The fuel is milled to obtain small particle sizes (< 2 mm) before entering the furnace together with the preheated primary combustion air. The combustion then takes place in suspension, at temperatures up to 1600 °C [13]. A small fraction of the fuel ash particles may end up in the bottom ash, while most of the fly ash particles formed will be transported through the furnace with the flue gas [13]. Table 3 lists the ash related measuring campaigns conducted and the type of examinations performed in biomass suspension fired boilers.

Table 3: Overview of the full-scale suspension fired experiments performed in Denmark

Ref	Year	Boiler	Place	Fuel	Method		Exan			
					Probe measurements	Mature deposit samples	Buildup-rate	Chemistry of deposits	Corrosion	Shedding
[12]	2004	Jordbro	SH	Wood	X		X	X		
[19]	2007	Amager	SH, TB	Straw + add	X		X			
[20]	2008	Avedøre 2	F	Wood /coal ash	X		X	X		
[9]	2011	Amager	SH, TB	Straw/wood	X		X	X		X
[21]	2011	Avedøre 2	F	Wood/coal ash	X		X	X		(X)
[22]	2011	Avedøre 2	F, SH	Wood/coal ash	X		X	X		(X)

Places: F = furnace, SH = near superheater, TB = Tube bank

In suspension fired units only probe deposits have been examined, until now. The focus of these examinations has been on the rate of deposit formation, chemistry of fuels, ash and deposits and shedding observations.

Two types of deposition probes have been applied in the conducted experiments. Both simple air-cooled probes, as well as more advanced probes for in-situ deposit measurements and soot-blowing have been applied. In the early experiments air-cooled probes were employed. An air-cooled probe is a stainless steel probe with thermocouples placed along the probe surface in order to control the probe temperature to a given set-point by adjusting the air flow-rate. The deposits mass is determined by extracting the probe after each experiment and subsequently remove the deposits for weighing and analysis [5,7].

In later studies, an advanced in situ shedding probe has been utilized, see Figure 1. The in situ deposit probe is constructed of a double annular tube which ensures a uniform cooling of the probe by water and compressed air in counter-current flow. The probe is equipped with a load cell, and online quantification of mass and heat uptake is possible. The flue gas temperature can be measured, both by a thermocouple and by a nearby suction pyrometer, and the deposit formation and shedding can be observed by a video camera [9,10,16,21,22].

In a few experiments [16,23] a soot blower probe was used along with the in situ deposition probe, in order to provide information of the removability of the formed deposits. The soot blowing probe is a simple probe equipped with a nozzle for ejecting high-pressure air at the end of the probe.

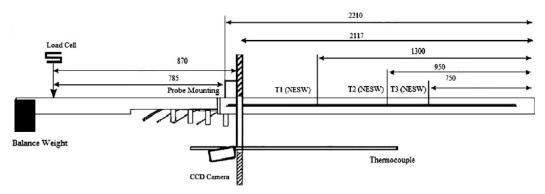


Figure 1: Advanced probe [9]

By adjusting the air pressure through the nozzle and the distance between the soot blowing probe and the deposits, the force needed for removal of deposits can be determined [16,23]. In Figure 2, three methods of applying the soot blowing probe near the deposit probe are illustrated.

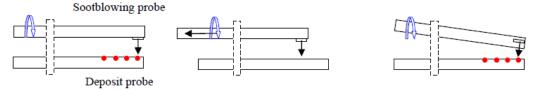


Figure 2: Application of the soot blowing probe [24]

#### 3 RESULTS AND DISCUSSION

The results obtained in the full-scale measuring campaigns will be reviewed and compared in this section. The focus is the rate of deposit formation, the chemistry of deposit and the observations on shedding. When examining the full-scale experimental results, it should be kept in mind that full-scale boilers are not very well-controlled with respect to operational parameters. Large variations in flows, temperatures, fuel compositions etc. may occur within a relatively short time. Thus, at best only major influences of operational parameter changes may be observed.

#### 3.1 RATES OF DEPOSIT BUILD-UP

The rate at which the deposits are formed in a biomass-fired boiler is important, since a decrease in the heat transfer from the flue gas to the steam cycle may be associated with an increase in deposit mass [2].

When looking at the rate of deposit formation  $[g/m^2/h]$ , two definitions of the buildup-rate of deposits have been employed, (i) the Integrated Deposit Formation rate (IDF-rate) and (ii) the Derivative-based Deposit Formation rate (DDF-rate), as defined by Bashir et al. [10].

The IDF-rate is determined by determining the deposit mass on the probe, at a given time after the probe is introduced to the boiler. The deposit mass is then divided by the probe surface area and the time of exposure, and the rate  $[g/m^2/h]$  is determined. By this method the build-up rate may be influenced by shedding events, by which deposit is removed from the probe.

The DDF-rate can be obtained by monitoring the mass uptake signal from the advanced probe. The DDF-rate is determined by calculating the time derivative of the deposit mass uptake between two shedding events [g/h] as illustrated in Figure 3.

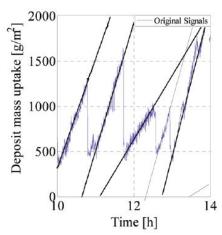
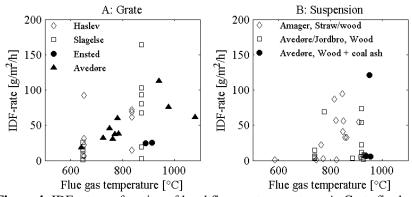


Figure 3: Original signal and determination of DDF-rate. Adapted from [10]

The rate  $[g/m^2/h]$  is then obtained by dividing the time derivative by the probe surface area. By this method only small shedding events which cannot be separated from the measuring noise are included in the build-up rate. The DDF-rate has mainly been employed in recent studies on suspension firing [10,21,22].

In Figure 4, the IDF rates measured are seen as function of local flue gas temperature for grate (or cigar) fired and suspension fired units.



**Figure 4:** IDF rates as function of local flue gas temperature. A: Grate fired units, all straw fired. Probe temperatures are 510 °C in Haslev and Slagelse, 650 °C in Ensted and 400-650 °C in the Avedøre grate boiler [5,16,17]. B: Suspension fired units. Probe temperatures are within 470-590 °C in Amager [9,10], 520 °C in Jordbro [12] and 550 °C in the Avedøre suspension boiler [20,22].

It is seen that for grate fired units there seem to be some influence of the flue gas temperature on the deposit build-up rate. The probe temperatures vary within 400-650 °C in the experiments, with most probes set to around 500 °C. The influence of probe temperature has been examined by Jensen et al. [16], with the conclusion that the probe temperature has limited influence on the deposit formation rate.

For suspension fired units, it can be seen in Figure 4B that the data are rather scattered. For these data, it should be noted that they are obtained in quite different scenarios, both with respect to boiler configuration and fuel type.

It can be observed from Figure 4, that the IDF-rates for grate and suspension fired units are comparable, as most IDF-rates are in the range 0-100 g/m<sup>2</sup>/h for both

technologies. This observation is surprising since during grate firing only up to 20 wt% ash is entrained while 80-90 wt% of the ash is expected to end up in the fly ash during suspension firing [14]. For the cigar fired unit, the entrainment is considered to be higher than in grate-fired units [5].

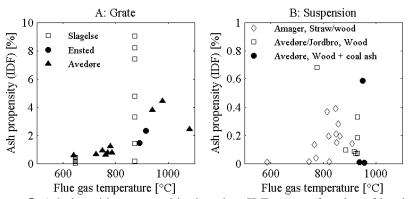
In order compare the deposit buildup for different fuel and combustion systems an ash propensity has been calculated. The ash propensity is defined as:

Ash propensity [%] = 
$$\frac{\text{Deposit flux } [g/m^2/h]}{\text{Ash flux } [g/m^2/h]} \cdot 100\%$$

The deposit flux is the IDF- or the DDF-rate, while the ash flux describes the local ash flow near the probes. The ash flux is calculated by:

Ash flux 
$$[g/m^2/h] = \frac{\text{Fuel flow } [g/h] \cdot \text{Ash content} \cdot \text{Entrainment}}{\text{Cross sectional area at probe position } [m^2]}$$

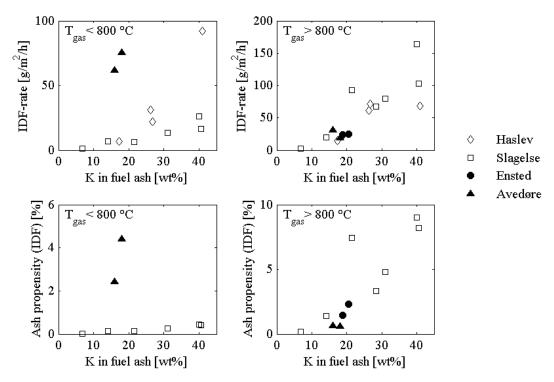
The ash content and the entrainment are given as fractions. Calculation of the ash flux has to rely on some assumptions. The fuel flow in the boilers is assumed to be equal to full load of the boiler, unless stated otherwise in the references. The ash content of the fuel is in all references either provided by analysis of the actual fuel or assumed based on earlier fuel analyses at the plant. The boiler dimensions at the probe positions have been obtained by communications with the owners of the boilers (DONG Energy or Vattenfall A/S). The cross-sectional area of the Haslev cigar boiler is currently unknown for the authors. The fraction of ash entrained may vary in the different boilers and can only be roughly estimated. It is assumed that in suspension fired units, the entrainment is 80 % of the fuel ash, while in grate fired units the entrainment is assumed to be 10 %, based on a mass balance provided in ref. [16]. The calculated ash propensities based on IDF-rates are seen in Figure 5.



**Figure 5:** Ash deposition propensities based on IDF rates as function of local flue gas temperature. A: Grate fired units, all straw fired [5,16,17]. B: Suspension fired units [9,10,12,19,20,22]. Probe surface temperatures are described in Figure 4.

It is seen that the ash deposition propensities are much higher for grate fired units than for the suspension fired units. For grate fired units up to 10 % of the ash entrained may deposit on the probe, while for suspension fired units only up to 1 % is deposited. Most of the data is below 0.5 % for suspension-firing. The difference in the ash propensities of the two combustion systems may be explained by differences in the chemical composition of the fly ash, which will be examined later.

It is seen in Figure 4A and Figure 5A that for grate-fired boilers the IDF-rate and the ash deposition propensity increase with the local flue gas temperature. However, as can be seen in the scattering of the data from Slagelse (marked with  $\Box$ ), obtained at the same temperature, other parameters also influence the rate of deposit formation. In Figure 6, the influence of the ash propensity or IDF rate is seen as function of the fuel ash content from the measuring campaigns where the fuel ash was sampled before each experiment [5,16,17].

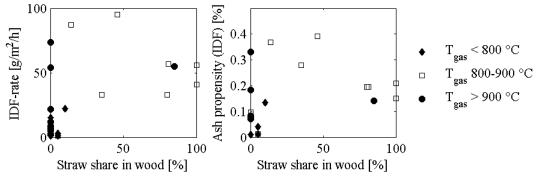


**Figure 6:** IDF rates (upper figures) and ash propensities (lower figures) as function of the fuel ash K content for grate boilers. Left figures; Flue gas temperatures < 800 °C. Right figures; Flue gas temperatures > 800 °C. Probe temperatures: Haslev and Slagelse = 510 °C, Avedøre and Ensted = 650 °C. Data from refs [5,16,17]

It is seen that there is a correlation between the K-content in the fuel ash and the deposit formation rate whether this is expressed as an IDF-rate or an ash deposition propensity. In the upper figures showing the IDF-rates it is seen that the data from Haslev and Slagelse each may follow linear correlations, as also found in the original work [5]. In the lower figures, the ash deposition propensities are shown, and data from different boilers can be compared. For flue gas temperatures lower than 800 °C (lower left figure), it is seen that there is quite a difference in the data from Avedøre and Slagelse. This may be due to differences in probe temperatures (500 °C at Slagelse vs. 650 °C at Avedøre), which may have a rather significant effect at low flue gas temperatures (650-760 °C). For flue gas temperatures above 800 °C (lower right figure), obtained in or near the furnaces of the plants, it is seen that there is a correlation between the K-content in the fuel ash and the ash deposition propensity which may apply to all grate fired plants included in the comparison. In these data, there are also differences in the probe temperatures (510 °C vs. 650 °C), but this seems to be of minor importance at these higher flue gas temperatures.

For grate fired units it seems that an increased deposition rate can be expected when the fuel ash K-content and the flue gas temperature are increased.

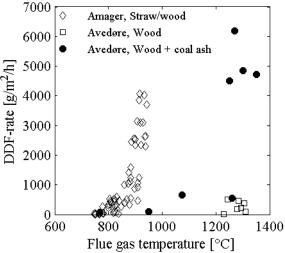
For suspension firing, a rather large scattering of data was observed whether the IDF-rate (Figure 4B) or the ash propensity (based on IDF-rates, Figure 5B) was shown as function of flue gas temperature. In the experiments performed on suspension firing, chemical analysis of the fuel mixture is not conducted before each experiment, so the IDF-rate cannot be correlated to the K-content of the fuel as was done for the grate fired units. The influence of fuel composition is however examined by plotting the IDF-rate as function of the straw share in wood, which is estimated from measured ash fractions. See Figure 7. The experiments with wood with coal ash addition are excluded from the comparison.



**Figure 7:** IDF rate (left figure) and ash propensity (right figure) in suspension fired units as function of the straw share in wood. Data from Jordbro [12], Avedøre [20,22] and Amager [9,10,19].

It seems as if the fuel composition influences the rate of deposit formation. However, any clear trend cannot be determined based on these rather scattered data.

In recent measuring campaigns, where the advanced probe was used, the DDF-rate was calculated by only including the deposit mass change between major shedding events. The DDF-rates are seen as function of flue gas temperature in Figure 8.



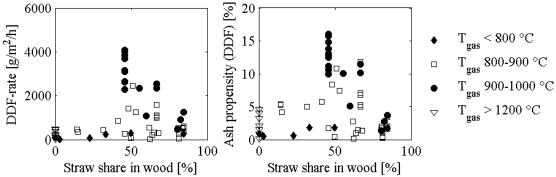
**Figure 8:** DDF-rate vs. flue gas temperature for suspension fired boilers. The probe surface temperatures are within 470-590 °C. Data from refs [10,21,22]

It is seen that there are more data available for the DDF-rates, than for the IDF-rates. This has two explanations; the DDF-rate is calculated several times during each experiment, while only one IDF-rate is obtained, typically for the first 12 hours.

Secondly, in some experiments complete shedding of the deposits are observed. In that case it does not make sense to calculate an IDF-rate. This behavior is observed for wood and wood with coal ash combustion at high temperatures > 1100 °C.

It is seen in Figure 8 that for the straw/wood fuel mixture and the wood with coal ash addition, there seem to be a correlation between the DDF-rate and the flue gas temperature, as the rate of deposit formation increases when the flue gas temperature increases. The temperature dependence is however not similar for the three fuel mixtures. The data with the straw/wood fuel mixture are obtained with flue gas temperatures in the range 750-950 °C. However, combustion of wood at much higher temperatures, above 1200 °C, resulted in much lower deposit formation rates. It thus seems that other parameters than the flue gas temperature has an effect on the deposit formation rate.

The influence of fuel composition is examined by plotting the DDF-rate or ash propensity (based on the DDF-rate) as function of the straw share in wood. The experiments where wood with coal ash addition is used as fuel are excluded from the comparison.



**Figure 9:** DDF rate (left figure) and ash propensity (right figure) as function of the straw share in wood for suspension firing. Data with pure wood (0 % straw) from Avedøre [22], other data from Amager [10]

It is seen that there may be higher DDF-rates and ash deposition propensities when the straw share exceeds 50 % as compared to fuels with lower contents. It however seem as if the deposition rates are more influenced by differences in the flue gas temperatures and the influence of fuel composition on the deposit formation may be limited compared to the influence of temperature.

The difference in the temperature dependence for the various fuels observed in Figure 8, may thus also be caused by other differences in the boilers, as these are quite different in construction.

When examining the IDF- and DDF-rates obtained for suspension firing, the temperature seems to influence the DDF-rate, while the fuel composition mainly seem to influence the IDF-rate, though no clear correlation could be detected.

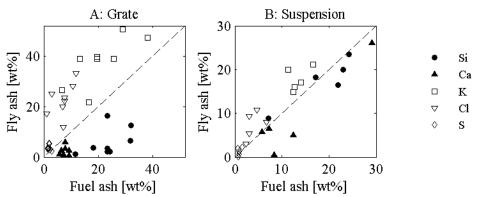
That the fuel composition seems to have a larger influence on the IDF-rate than on the DDF-rate may be explained by the fact that major shedding events may be included in the determination of the IDF-rate and will thus have a large impact on the IDF-rate and not on the DDF-rate. The chemistry of ash and deposits may have more influence on the strength of the deposit and thus on the shedding than on the deposit formation. Contrary, the flue gas temperature may influence the build-up rate more than the shedding rate, possibly through influences on the physical state of the ash particles.

#### 3.2 CHEMISTRY OF ASH AND DEPOSITS

It was seen in the previous section, that the deposit formation rates (IDF) was on similar levels for grate and suspension-fired units (Figure 4). This was explored further by examining the ash propensity of the two systems (Figure 5) and it was found that for grate-fired units up to 10 % of the incoming ash may deposit on the probe, while for suspension-fired units only up to 1 % is deposited (based on IDF-rates). The ash in grate-fired units is thus more prone to end up as deposits than the ash in suspension-fired units. As the flue gas temperatures in the systems were similar at the probe positions, the difference may be caused by chemical differences of the fly ashes. Such differences will also lead to differences in the chemistry of the deposits formed. In this section the chemistry of the fly ash and deposits will be reviewed along with influences of operational parameters.

## 3.2.1 FLY ASH CHEMISTRY

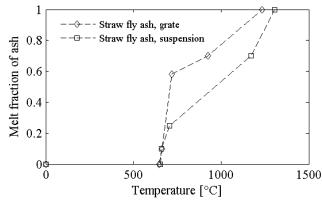
The firing technology will have great impact on the fly ash formation due to differences in entrainment etc. In Figure 10, fuel and fly ash compositions are compared for each of the two firing technologies, grate and suspension firing, to gain an idea on how the ash transformations occur in or near the combustion zones. The chemical examinations in this work mainly focus on the five major ash forming elements in biomass combustion; Si, Ca, K, Cl and S.



**Figure 10:** Fly ash composition vs. fuel ash composition. Points on or near the diagonal line indicate that the fuel and fly ash compositions are similar. A: Grate; fuels are straw from refs [5,17]. B: Suspension. Fuels are various straw/wood mixtures from refs [9,10,12]

It is seen that for grate-firing, the fly ash composition is quite different from the fuel ash composition, as almost no points are placed near the diagonal line. The fly ash is rich in K, Cl and S and depleted of Si and Ca compared to the fuel ash. This is contrary to suspension-firing, where the fly ash to a large extent resembles the fuel ash, as seen by the distribution of points close to the diagonal line. Only a slight enrichment of K, Cl and S is found in this combustion system. The difference in the fly ash formation behavior can be explained by the difference in entrainment of ash in the two combustion systems. As K, Cl and S are volatile elements in the fuel, these are to some extent released to the gas phase in the combustion zone, while Ca and Si are retained in the solid fuel (or ash) particles [1]. In grate-firing most of the solid ash particles remain in the bottom of the furnace and Ca and Si are thus only found in the fly ash to a limited extent. Contrary, in suspension-firing the ash particles are entrained to a large extent, which leads to the similar composition of the fuel ash and fly ash.

The differences of the chemical composition results in different melting behaviors and thereby stickiness of the fly ash particles as well as of the formed deposits. Zhou [25] has presented empirical correlations for predicting the melt fraction of ashes as function of temperature based on the chemical analysis of the ash. The basis of the correlation is a number of ash melting tests performed on straw ashes [26], and it can thus not be expected to apply to wood ashes. The correlations have been used to calculate melting curves of fly ashes of straw from grate and suspension firing. The result is seen in Figure 11.



**Figure 11:** Predicted melting curves of fly ashes from grate and suspension firing of straw. Ash compositions from ref [9].

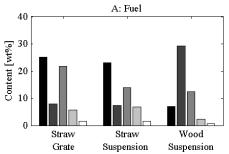
It is seen that there is significant difference in the predicted melt fraction of straw fly ashes in the temperature range 650-1300 °C, which can partly explain the difference in the deposition behavior observed for grate- and suspension-fired units.

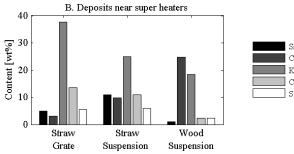
The differences in ash deposition propensity may furthermore be caused by the physical form of the fly ashes, which may be quite different in the two combustion systems. In grate fired units, K and Cl dominates the fly ash composition and is expected to be found as KCl vapors or aerosols, which will easily stick to heat transfer surfaces. In suspension fired units K and Si dominates and are mainly found as solid K-silicates [1].

#### 3.2.2 DEPOSITS CHEMISTRY

The deposits are formed from the fly ash and the deposit chemistry is thus influenced by both the formation of fly ash and the ability of the fly ash to deposit on heat transfer surfaces. In the following it will be reviewed how the chemical transformations occur in the two combustion systems based on the chemical analysis of fuels, fly ash and deposits collected in the measuring campaigns.

In Figure 12, the chemical composition (with respect to the five major ash forming elements) of deposits formed on probes near super heater tubes can be seen for three firing cases; straw in grate-firing, straw in suspension-firing and wood in suspension-firing. In Figure 12A the ash compositions of the fuels used in the three cases are seen. It is seen that the two straws are similar, though the straw fired in the grate boiler has a higher K content than the straw fired in suspension. The compositions of the deposits formed in the two cases of straw combustion are seen in Figure 12B. It is seen that the deposits from suspension firing contains more Ca and Si and less K than the deposits from grate firing. This is as could be expected based on the fly ash chemistry examined previously. Two cases of suspension firing are seen in Figure 12; with straw and with wood as fuel, respectively. In Figure 12A it is seen that there are





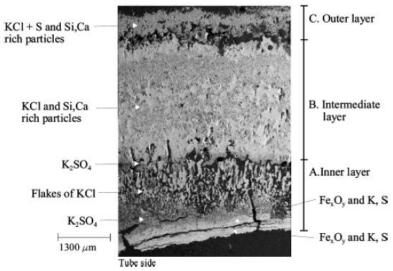
**Figure 12:** Corresponding fuel and deposit compositions in three firing cases. The fuel ash compositions are seen in the left figure, while compositions of the corresponding deposits are seen in the right figure. Data for straw in grate-firing [5], pure straw in suspension firing [9] and for pure wood in suspension firing [12]

differences in the fuel ash compositions of the two fuels. Wood contains more Ca and less Si and Cl than straw. These differences are also found in the compositions of the deposits as seen in Figure 12B.

In Figure 12, the deposits chemistry has been provided as a bulk chemical composition. In reality, the deposits are composed of layers, with different structures and possibly also chemical composition. Furthermore, there are differences in the deposits on the upstream and downstream side of the probe. The upstream side means the half circle of the probe facing the flue gas direction.

For grate fired units, both probe deposits and mature deposit samples from superheater tubes have been examined with respect to chemistry and morphology.

In Figure 13 a SEM photograph of a mature upstream deposit cross-section from the Ensted straw fired grate boiler is seen. The mature deposit is collected from a super heater tube at a position in the boiler where the flue gas temperature is < 900 °C. The super heater steam temperatures are within 389-470 °C at the sample position [15].



**Figure 13:** SEM photograph of the layered structure of a mature super heater deposit collected at the Ensted straw fired grate boiler. From ref. [15]

The layered structure is clearly seen in Figure 13. The innermost layer is found on top of an iron oxide scale of the super heater tube. The layer is composed of sub layers of K<sub>2</sub>SO<sub>4</sub> and KCl flakes. The intermediate layer of the mature deposit contain many Siand Ca-rich particles, which are glued completely together by KCl, and the layer is

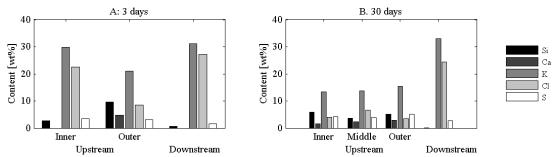
thus quite dense. The outer layer also contains Si- and Ca-rich particles glued together by KCl and also by K<sub>2</sub>SO<sub>4</sub>. The outer layer is however very porous [15].

Mature deposit samples have also been collected from the super heater tubes of the Masnedø straw fired grate boiler. In this boiler the steam and flue gas temperatures at the sample position is higher than in the Ensted boiler (387-521  $^{\circ}$ C and 960-1019  $^{\circ}$ C, respectively). In this boiler the innermost layer is also composed of KCl and K<sub>2</sub>SO<sub>4</sub>, but the distribution of these two compounds in the sub-layers varied, without any systematic variation with steam temperatures at the sample location. The intermediate layer contained almost no chlorine which is explained by the higher temperatures of the Masnedø boiler. The outer layers of the deposits collected in Masnedø was quite similar to the outer layers collected in Ensted, both with respect to morphology and chemistry [15].

The K/(2S+Cl) molar ratio of the layers from the two boilers have been calculated from the chemical analysis to determine whether the K is present in other forms than KCl and  $K_2SO_4$ . It is found that the ratio is  $\approx 1$  for the innermost layer and K is thus only expected to be found as KCl and  $K_2SO_4$ . In the intermediate and outer layer the ratio is above 1 and K can be expected to be found in other forms [15].

The chemical composition of the mature deposit samples are found to be quite similar to the chemical composition of the deposits collected on probes in straw fired grate boilers [15]. The morphology is however quite different, especially for the inner layers. The deposits on probes have a thinner and less dense inner KCl layer compared to the mature deposits. The inner layer of probe deposits from straw fired grate boilers is typically followed by a porous KCl-rich layer and then by an outer layer of Si- and Ca-rich particles glued together by KCl [15].

In Figure 14 the chemical compositions of two probe deposits obtained in the Avedøre straw fired grate boiler in 3 and 30 days, respectively, are seen [16].



**Figure 14:** Chemical composition of deposit layers collected at the Avedøre straw fired grate boiler with a 500 °C probe where the flue gas is within 700-800 °C. From ref. [16].

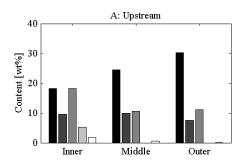
It is seen that the deposit accumulated in 3 days is only composed of two layers. These are described as a thin (0.5-1 mm) inner white and powdery layer and a 5 mm outer grey layer, which is quite hard. It is seen in Figure 14A that the inner layer is composed of mainly K and Cl, while the outer layer also contains some Si and Ca.

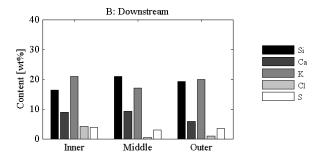
When the exposure time of the probe is increased to 30 days in the same conditions, differences in the deposit structure can be observed as seen in Figure 14B. The deposit then contains three layers. These are described as an inner layer similar to the short-time probe deposit, although slightly grey. The intermediate layer is a 1-3 mm grey and hard layer, while the outer layer is a 1-2 mm grey, porous and powdery layer. The 30 days deposit thus has a greater resemblance with the mature deposits.

Looking at the chemical compositions of the deposits from the two exposure times in Figure 14, it is seen that there are only limited differences, mainly in the composition

of the inner layer, which contains more Si, Ca and S at the long exposure time. It thus seem like time has an influence on the morphology of the deposits more than on the chemical composition. The deposits on the downstream side of the probe are found be composed of K and Cl and to be unaltered with the longer exposure time, both with respect to chemistry and morphology [16].

For suspension firing, no analysis of mature deposits is available at this point. Bashir et al. [10] has made a detailed analysis of the deposit layers formed on a probe during suspension firing of a straw/wood mixture containing at least 46 wt% straw. The chemical analysis with respect to the 5 elements of interest is seen in Figure 15.

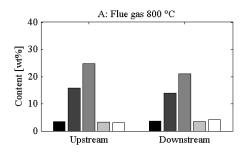


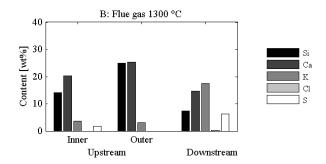


**Figure 15:** Chemical composition of deposit layers collected at the Amager straw/wood fired suspension boiler with a 500 °C probe where the average flue gas temperature is 876 °C [10].

It is seen in Figure 15 that the deposit from suspension firing has much higher contents of Si and Ca in all parts of the deposit than what has been observed for straw grate-firing. This difference may occur due to the presence of wood in the fuel mixture and/or due to shift of firing technology. It is seen that only the inner upstream layer and the downstream layers have significant amounts of K, Cl and S. The K/(2S+Cl) molar ratio is in all layers > 1, indication that K is present in other forms than as KCl and  $K_2SO_4$ . SEM-EDS analysis conducted on the upstream outer layer of deposits formed during combustion of pure straw [9] indicate that molten particles rich in K, Ca and Si are found within the deposit along with smaller particles rich in K, S and Ca.

Analysis of the deposit layers has also been conducted for deposits obtained on a probe during suspension firing of wood at two temperatures in the Avedøre suspension boiler. The result is seen in Figure 16.





**Figure 16:** Chemical composition of deposit layers collected at two positions in the Avedøre wood fired suspension boiler with a 550 °C probe temperature. From ref. [22].

The chemical analysis seen in Figure 16 is supported by SEM-EDS analysis of the deposits [22]. For the deposits obtained in the super heater section where the flue gas temperature is around 800 °C (Figure 16A), the morphology and the chemical

composition of the deposits on the upstream and the downstream side of the probe is quite similar. Only one deposit layer is obtained due to limited deposition occurring at these conditions. The deposits are composed of mainly K and Ca, but also Cl and S appears. The deposits are found to be clusters of very small particles. For the downstream deposit all the K is found to be water soluble, while the water soluble part is 88 % of the upstream deposit. It is found that only part of the soluble K (40-60 %) is found as sulfates and chlorides. The rest is expected to be found as other water soluble compounds such as KOH or  $K_2CO_3$  [22].

These deposits obtained with wood and flue gas temperatures at 800 °C are thus quite different from the deposits obtained with a straw/wood mixture at an average flue gas temperature of 876 °C seen in Figure 15. In the super heater deposits obtained with the straw/wood mixture, ash particles composted of K, Ca and Si was found in the deposits. These were not found in the deposits obtained with wood, except for very few ash particles in the downstream deposits.

In the Avedøre suspension fired boiler a deposit probe was also placed in the furnace, below the screen, where the flue gas is  $1300\,^{\circ}$ C. The compositions of the deposits collected on the probe are seen in Figure 16B. It is seen that the layers of the upstream deposits are quite different. The outer deposit is dominated by Si, Ca and K, while the inner deposit also contains S. Common for the two layers is the presence of spherical ash particles composed of Si, Ca and K, and partially melted particles rich in K and Si. The K in the outer layer is insoluble and thus found as K-silicates, K-Al-silicates or K-Ca-silicates. In the inner layer 40 % of the K is water soluble and found as mainly  $K_2SO_4$  [22]

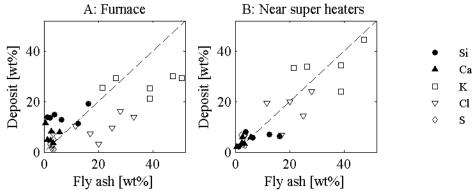
The downstream deposits obtained at 1300 °C contain a lot of S-species, likely K<sub>2</sub>SO<sub>4</sub>, which is partially melted or found as small particles. Besides this, also spherical particles of K, Si and Ca are found along with molten particles of K and Si. Most of the K is water soluble and some is expected to be found as KOH or K<sub>2</sub>CO<sub>3</sub> [22].

It is seen in this section that time influences the structure of the deposits, with respect to number of layers and to the thickness and morphology of the individual layers. The layers become thicker and denser with increased exposure time. The exposure time on the other hand do not seem to influence the chemistry of the deposits. These influences of time are seen by comparison of mature deposits with probe deposits and comparison of two probe deposits obtained with short and long exposure times, respectively. The firing technology is seen to influence the chemical composition of the deposit. Deposits obtained in suspension fired units contain more Si and Ca than deposits obtained in grate fired units with a similar fuel. The differences apply to all layers of the deposits and can be explained by differences in the fly ash formation. The choice of fuel naturally also influences the chemistry of deposits. Deposits from suspension firing of straw contain Si, Ca, K and Cl, whereas deposits from wood firing are dominated by Ca and K. This is explained by the differences in fuel ash chemistry. It is found that deposits from wood suspension firing almost don't contain fly ash particles, contrary to deposits from straw suspension firing obtained at similar temperatures. It is possible that this may be explained by differences in the melting behavior of the ashes or by lower ash contents of wood, leading to lower ash fluxes. It is estimated that in the examined experiments the average ash flux in the straw/wood fired suspension boilers is 18000 g/m<sup>2</sup>/h at the probe position. The average ash flux for the wood fired experiments is only 8100 g/m<sup>2</sup>/h. Flue gas temperature is also observed to influence the deposit morphology and chemical composition. The influence of temperatures will be examined further in the following section.

#### 3.2.3 INFLUENCE OF TEMPERATURE ON DEPOSITS CHEMISTRY

It was seen in the previous section that the deposits are influenced by the local flue gas temperatures as differences in the deposit composition was quite different in two places of a wood fired suspension boiler. For grate fired boilers, the chemistry of deposits at different boiler positions has also been examined.

In the measuring campaign conducted in Haslev and Slagelse [5], the fuel and fly ash were sampled in each test along with deposits collected in two positions in the boiler. In Figure 17, the fly ash composition (also seen Figure 10A) is compared to the bulk compositions of the deposits formed in the furnace chamber at flue gas temperatures of 835 °C or 873 °C, and to the deposits collected near the super heaters at flue gas temperatures near 650 °C.



**Figure 17:** Deposit probe compositions vs. fly ash compositions in grate fired boilers. A: In the furnaces (835/873 °C). B: Near the super heaters (650°C). Data from Haslev and Slagelse [5]

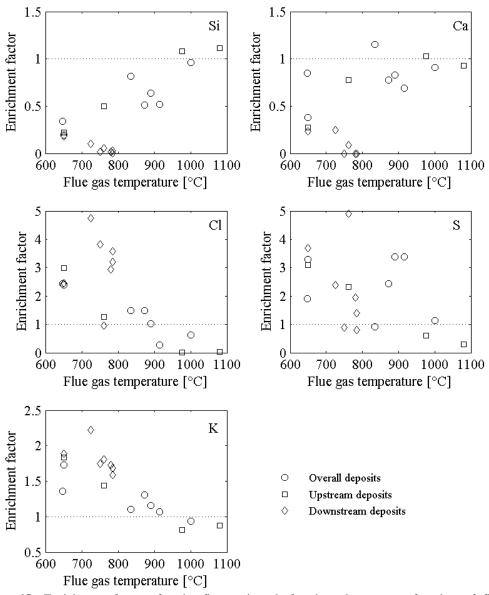
It is seen that in the furnaces (at high temperatures), the deposits contain more Ca and Si and less K and Cl compared to the fly ash. At the probes near the super heaters, where the flue gas temperature is 650 °C, the deposits chemical composition resembles that of the fly ash. There is thus a shift in the deposition behavior with flue gas temperature.

This has been explored further by calculation of an enrichment factor for each element;

Enrichment factor = 
$$\frac{\text{wt\% in deposit}}{\text{wt\% in fuel ash}}$$

In the calculation of the enrichment factor, the fuel ash composition is used rather than the fly ash composition, since the fuel ash composition has been examined in more measuring campaigns and is often known to a larger extent than the fly ash composition. It should be kept in mind when examining these data, that the enrichment factor is based on two ash splits; one split occurring in the combustion zone (especially for grate-firing) and one split occurring during deposit buildup, where the elements behave differently.

The enrichment factors for the five main ash forming elements in grate-firing of biomass are seen as function of flue gas temperature in Figure 18. It is seen that for Si and Ca, the enrichment ratio is low at the low temperatures and approaches an enrichment factor around 1 at higher temperatures, except for the downstream deposits. For Cl, the enrichment factor is high at low temperatures and then decrease with increasing flue gas temperatures. It seems that deposits formed at high flue gas temperatures can be expected to be depleted of chlorine. A similar behavior is observed for sulfur, though with a much larger scattering of data. The enrichment

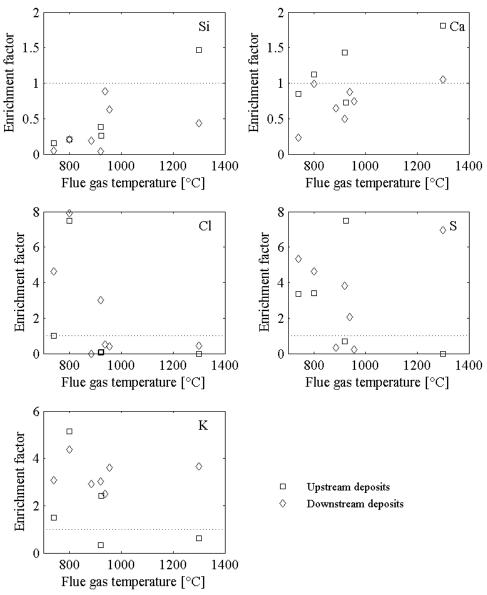


**Figure 18:** Enrichment factors for the five main ash forming elements as function of flue gas temperature for deposits collected in grate fired boilers; Haslev, Slagelse, Avedøre and Ensted [5,16,17]. The point shape indicate at which position on the probe, the deposits are collected; upstream means the half circle of the probe facing the flue gas direction.

factors for K are between 1 and 2 at the low flue gas temperatures. At higher temperatures the K enrichment factor decrease and approach 1.

The enrichments factors have also been calculated for the deposits collected on probes in suspension fired boilers. The results are seen in Figure 19. It is seen that the influence of the flue gas temperature on the enrichment factors is the same as observed for deposits from the grate fired units in Figure 18. The main differences observed among the enrichment factors from the two combustion technologies are that the enrichment factors of K, Cl and S are higher in suspension-fired units at the low temperatures. Furthermore, the downstream deposits can be expected to contain some Si and Ca, contrary to deposits from grate fired units. These differences can all be related to the higher entrainment of ash in suspension firing.

The influence of temperature on the deposits chemistry can be explained by the deposit mechanisms involved in deposit buildup.



**Figure 19:** Enrichment factors for the five main ash forming elements as function of flue gas temperature for deposits collected in suspension fired boilers [12,20,22]. The point shape indicate at which position on the probe, the deposits are collected; upstream means the half circle of the probe facing the flue gas direction.

The decrease in K, Cl and S enrichment factors with increasing flue gas temperature can be explained by limited condensation at high temperatures. The flue gas contains KCl and  $K_2SO_4$ , which may condense on the cold probe. The rate of condensation is determined by the difference in the flue gas concentration and the saturation concentration of KCl or  $K_2SO_4$  near the surface. The surface temperature of the deposit on the probe is determined by the flue gas temperature after some initial build-up has occurred. At high temperatures the saturation concentration is high and the gaseous species will not be transported toward the surface. This may explain the lower enrichment ratios of K, Cl and S observed at higher temperatures. The saturation concentration of KCl increases drastically around 700 °C, while the saturation concentration of K2SO<sub>4</sub> is low up to temperatures around 1100 °C [27]. This explains the differences observed between Cl and S, as these two elements are mainly transported to the deposits as KCl and  $K_2SO_4$ .

The increase in the enrichment factors of Ca and Si with increased flue gas temperatures can be explained by a higher melt fraction of the fly ash particles containing Si and Ca and of the deposit surface at high temperatures. When the melt fractions increases, the particles are more prone for sticking on the probe surface when the particles coincide with the surface by inertial impaction.

It has thus been found in this section that the flue gas temperature influences both the rate of deposit formation and the deposits chemistry. Large particles deposit by inertial impaction and the increase in deposit mass and change in bulk chemical composition is thus most pronounced for this mechanism. When the rate of inertial impaction increases with temperature, the rate of deposit formation is thus increased and the bulk chemical composition is changed toward higher contents of Si and Ca.

The influence of varied probe temperature has been examined in the measuring campaign at the Avedøre straw fired grate boiler [16]. The flue gas temperature was within 700-800 °C, while the probe surface temperature was varied within 400-550 °C. It is found that neither the deposition rate nor the deposit chemical composition is varied with these variations in probe temperature, except for the chlorine content of the deposit, which seem to be lowered at higher probe temperature. A similar conclusion is obtained by Michelsen et al. [6] at the Rudkøbing straw fired grate boiler. Probes with temperatures of 460 °C and 550 ° were found to collect deposits with similar chemical compositions. Deposits from an uncooled probe were however depleted of chlorine [6].

It is however found in both experiments that the thickness of the deposit is increased with increased probe temperature and that the morphology is altered. At high probe temperatures the deposits seem to have been molten to a larger extent [6,16]. The overall deposit patterns also changes with temperature; at 400 °C the deposit is uniform along the probe. At 500 and 550 °C a 'camel-back' like deposit was formed [16].

#### 3.3 SHEDDING OF DEPOSITS

The deposits formed on the surfaces in a biomass fired boiler may be removed by shedding events. Various types of removal mechanisms have been observed and these mechanisms have been reviewed by Zbogar et al. [3]. In Table 4, an overview of shedding mechanisms can be seen, where the place of shedding and the deposit type, with respect to the physical state is indicated for each mechanism.

**Table 4:** Deposit removal mechanisms along with indication of type of deposit and place at which the shedding occurs [3].

	Pla	ce of shedd	ing	Deposit type					
	Tube-								
	deposit	Within	Surface		Lightly	Heavily	Running		
	interface	deposit	removal	Powdery	sintered	sintered	slag		
Erosion			X	X	(X)				
Gravimetric	X	X		X	(X)				
Melting			X				X		
Thermally induced tensions	X	X			(X)	X			
- By combustion fluctuations									
- By load changes									
- By soot blowing									
Mechanically induced tensions	X	X		X	X	(X)			
- By 'natural' mechanical									
fluctuations									
- By soot blowing									

Erosion, gravimetric shedding, melting and to some extent also thermal tensions can be termed natural shedding mechanisms, while artificial shedding is often the result of induced thermal and mechanical stresses. As seen in Table 4, soot blowing may be a method for inducing mechanical or thermal tensions on formed deposits. Soot blowers operate by injecting jets of steam, water or high-pressure air into the boiler at positions where deposits are formed. The injection occurs through a nozzle located at the end of a long, rotating lance. The efficiency of the soot blower depends on the force of the jet, often given by the peak impact pressure (PIP) at a given distance from the nozzle and on the state of the deposit [16]. The thermally and mechanically induced tensions may lead to brittle fracture within the deposit or debonding from the tube surface, depending on the tensile strength of the deposit and the adhesion strength of the tube-deposit interface. The occurrence of shedding events is thus correlated to the strength development of the deposits. The strength can mainly be gained by either solidification of molten or partially molten material or by sintering of solid particles [3]. These processes depend on the temperature and the physical and chemical structure of the deposits.

The strength development and shedding of deposits has been examined to some extent for deposits formed during coal combustion and systematically for deposits in kraft recovery boilers, where the deposits are composed of alkali salts. Unfortunately only limited studies have been conducted in biomass fired boilers, and the experiences from coal and kraft recovery boilers can only be adapted to this fuel to a limited extent [3]. In the following the observations made in the Danish full-scale boilers firing biomass will be reviewed.

Shedding of deposits has been examined in grate fired units in two measuring campaigns, both conducted at the Avedøre straw fired grate boiler [16,18]. In one measuring campaign, a probe was placed in the top of the furnace chamber at the inlet to the superheater and the influence of flue gas temperatures in the range 800-1100 °C were observed with a probe temperature kept at 500 °C [18]. It was observed that the shedding of deposit took place by surface melting and droplet formation. It was found that the flue gas temperature governs the state of the deposit; at 900 °C and below, the deposits were solid. When the temperature increases to around 1000 °C, the deposits contain both melt and solid particles. At 1100 °C or above, the deposit surface layer is completely melted, and the deposits are rapidly removed as droplets [18].

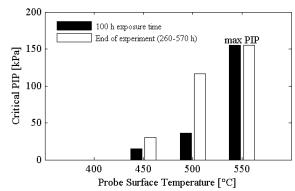
In the other probe measuring campaign conducted in the Avedøre grate-fired plant the probe was placed in convective section, where the flue gas temperature was within 700-800  $^{\circ}$ C.

During this measuring campaign at the Avedøre grate-fired boiler, the deposition behavior on the superheater tubes (SH1) near the probe has also been observed by camera. The temperature of the steam inside the tubes was around 400 °C and the tube metal temperature at this point can thus be assumed to be within 400-450 °C. The plant soot blower located near the tubes was approximately 1 m away, and the PIP of the jet at the tube is estimated to be 60 kPa [16].

In the first day after tube cleaning and boiler start-up a thin white layer accumulates on the SH tubes. In the second day a thick, snow-like deposit is formed. At seven days after startup the deposits on the upstream side of the probe is elliptical and dark grey. At the downstream side, the deposits are thin and slightly grey.

From this point forward no effect of the plant sootblowing can be detected and in the following weeks the deposits grow and bridging deposits between tubes were formed. The deposit behavior on the SH tubes is found to be in qualitative agreement with the behavior of the probe deposit [16].

During the experiments with the probe, the probe surface temperature was varied in the range 400-550 °C [16]. A soot-blower probe was used along with the deposit probe, and thereby the needed peak impact pressure (PIP) for removal of the deposits could be determined. A critical PIP was defined as the needed PIP for removal of more than 75 % of the deposit on the probe. In Figure 20 the needed PIP measured after 100 hour exposure times (4 days) and just before the probe is removed at the end of the experiment (260-740 hours exposure time) are seen.



**Figure 20:** Critical PIP for removal of front deposit for different probe surface temperatures and exposure times. At 550 °C less than 25 % deposits are removed at max PIP. From ref [16]

As seen in Figure 20, the probe temperature and the exposure time influence the removability of the front deposit. Higher probe temperatures and long exposure times lead to deposits which are difficult to remove.

This is considered to be due to sintering and thereby increased deposit strength and increased deposit-tube adhesion strength. The mechanism of removal is in all cases brittle fracture and debonding induced by the sootblower.

For the deposits at the downstream side of the probe it was found that these were easily removed, except those at the high temperature, 550 °C [16].

The upstream and downstream deposits are found to have differences in the chemical composition as the downstream side is mainly composed of K, Cl and S while the upstream side also contains some Si and Ca. As the deposits on the two sides of the probe can be expected to have similar temperatures within one experiment, it is considered that the chemistry of deposits also influences the strength and removability of deposits, since the shedding behavior is different at the two sides of the probe.

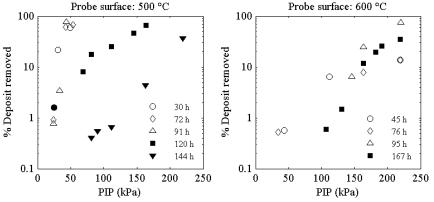
For suspension fired boilers, shedding has been examined for straw/wood mixtures [23,24], for wood [22] and for wood with coal ash addition [21; 22].

In the measuring campaign with straw/wood mixture as fuel [23,24], the probe was placed just above the screen tubes, where the flue gas temperatures are within 600-1050 °C. The influence of several parameters on shedding was examined with the advanced in situ deposition probe. Also in some cases a soot blower probe was used to determine the needed PIP to remove the deposit.

In the straw/wood fired boiler, shedding was observed to take place by debonding as natural shedding (when no soot blowing was applied) and as soot blower induced shedding. Furthermore, shedding by erosion caused by impaction of non-sticky particles was observed by visual inspection of the probe during operation. Shedding by probe deposit surface melting was not observed, even though the flue gas temperature was above 1000 °C during periods of the tests [24,23].

The mass uptake signal from the advanced probe used in the suspension fired boiler has been examined along with temperature measurements and boiler operational data to identify the parameters influencing the shedding. The shedding has been observed by three measures; the shedding rate  $[g/m^2/h]$ , the mass shedded in an event  $[g/m^2]$  and the shedding frequency  $[h^{-1}]$ .

It is found that when the flue gas temperature or the deposit mass on the probe are increased (>850 °C and >5000 g/m<sup>2</sup>, respectively) the shedding size is not significantly changed. The mean sizes of shedding events are 716 g/m<sup>2</sup> and 805 g/m<sup>2</sup> for natural and soot blower induced shedding events, respectively. The mean shedding frequency is however increased from 1.0 to 1.9 times per hour for natural shedding as the deposit mass load on the probe is increased from below to above 5000 g/m<sup>2</sup> (flue gas temperature > 850 °C). The increase in the shedding frequency leads to an overall increased shedding rate with increased flue gas temperature and deposit mass load. Although the shedding rate increases, the percentage of deposit removed in a shedding event decrease, since the amount shedded is relatively stable. It is generally observed that the shedding rate is lower than the DDF-rate, which implies that more and more deposits are attached to the probe and less and less can be removed as buildup time goes by [23]. It is considered that at high temperatures partial melting of the deposits occur, the deposit sinter and thereby the adhesion strength is enhanced. It is furthermore seen that at high temperatures the deposit layers are thicker and the upstream and downstream layers are connected, making the debonding more difficult. The influence of straw share in wood and of the probe surface temperature has also been examined. It is found that straw share (above or below 20%) does not have a significant impact on the shedding rate. The shedding rate is however in most cases higher at 500 °C than at 600 °C probe temperature, both for natural and soot-blower induced shedding. The influence of probe surface temperature and exposure time on deposit shedding has been examined by applying the soot blower probe. The influences have been examined by tracking the PIP of a sootblower jet needed for removal of deposits at various conditions [23]. The results are seen in Figure 21.



**Figure 21:** Percent deposits removed as function of Peak Impact Pressure and residence time. The deposit mass load on the probe increases with exposure time. From ref [23].

It is seen that at 500 °C probe surface temperature, the needed PIP increases with exposure time. Contrary, at 600 °C probe surface temperature, the exposure time is less significant and the deposits are difficult to remove even at short residence times. These results are in line with the results obtained in the straw fired grate boiler, discussed earlier.

Shedding observations has also been made for suspension-firing of wood, where probe observations and measurements with a 550 °C probe has been made in two positions in the Avedøre suspension-fired boiler [22]. The probe was placed in the furnace, just below the radiation shield and in the superheater section. At these positions the flue gas temperatures are approximately 1300 °C and 800 °C,

respectively. In the superheater section, where the flue gas temperature is  $\approx 800^{\circ}$ C the deposit mass uptake is slow. After some time, the deposit mass on the probe becomes constant, indicating equilibrium between deposition and shedding rates. The type of shedding at this position is not identified, but due to insignificant mass loss, it is probably not by debonding [22]. A possible mechanism could be erosion, but this has not been verified. At the location with flue gas temperatures around 1300 °C, the deposit buildup was fast and many shedding events with almost complete removal of the deposit by debonding took place [22].

It can thus be concluded that the shedding behavior is quite different from what is observed with the straw/wood mixture as fuel and that a thick layer of deposit were never established on the probe.

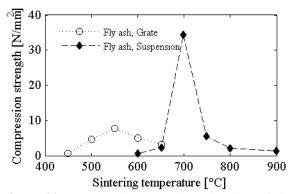
The effect of adding coal ash to the wood in a suspension fired boilers has also been tested, with applied coal ash to wood ash ratios within 3.6 to 7.4 [21,22]. It was found that the overall deposition and shedding patterns are similar at the two positions with flue gas temperatures 800 and 1300 °C with the addition of coal ash. It is however observed that at the 800 °C position, the constant amount of deposit obtained is lower than observed for the pure wood firing. The deposits obtained with coal ash addition were furthermore found to be easier to remove from the probe after the experiment. At the position with flue gas temperatures around 1300 °C, it was found that the build-up/complete shedding cycle is shorter than observed for wood firing. Without coal ash addition the cycle is approximately 10 hours, whereas adding coal ash leads to a cycle of approximately 2 hours [22]. The coal ash addition thus has a positive effect.

Shedding behavior has thus been studied in four cases of biomass combustion; (i) straw fired grate boiler at high flue gas temperatures, (ii) straw fired grate boiler at low flue gas temperatures and varied probe temperatures (iii) suspension firing of straw/wood at a range of flue gas and probe temperatures and (iv) suspension firing of wood at high and low flue gas temperatures.

It is observed that in straw fired grate boilers, the flue gas temperature largely determines the type of shedding occurring as shedding by melting is observed at high flue gas temperatures. At lower temperatures shedding only occurs by soot-blowing and the removability of the deposits is influenced by the probe surface temperature.

For suspension fired units firing wood possibly mixed with straw, no shedding by melting has been observed even at temperatures up to 1300 °C. Instead, shedding by debonding seems to be the primary deposition mechanism at high temperatures, both for straw/wood mixtures and pure wood as fuel. At lower flue gas temperatures at around 800 °C, two different observations are made. In the case of straw/wood mixtures as fuel, shedding by debonding is observed. When pure wood is fired in a different boiler a steady deposit mass is obtained on the probe. Shedding by debonding does not seem to occur in this case. Whether this difference in shedding behavior at the low temperatures is caused by the chemical differences of the deposits observed in Section 3.2.2 or by operational parameters of the two boilers is unknown at this point. From these shedding studies, it seems that both fuel composition and operational parameters, especially temperature, are important parameters in the shedding behavior of deposits.

In order to gain knowledge on the sintering behavior and the strength increase of deposits, lab-scale studies have been conducted. In these studies the compression strength of fly ash pellets from straw firing in suspension and on grate has been compared [16]. This is done by heat-treating fly ash pellets at different temperatures for 4 hours before the compression strength of the pellets are measured. The results are seen in Figure 22. It is seen that in both cases the compression strength first



**Figure 22:** Compression strength as function of sintering temperature for two fly ashes from straw combustion [16].

increases, then decreases as temperature is increased. The increase of compression strength is associated with sintering of the ash pellets, while the decrease in strength is associated with the formation of pores, due to evaporation of some elements. This behavior may not apply completely to real deposits, where long exposure times, additional deposition and possibly collapse of deposits may alter the sintering behavior.

However, it is seen that for the fly ash from suspension-firing the onset of strength increase is high (650 °C) compared to that of fly ash from grate-firing of straw (450 °C). The examined fly ash from suspension firing has a high content of Si and Ca, and a low content of K and Cl compared to the fly ash from grate-firing [16]. It is thus seen that both the chemical composition and the local temperature influences the deposit strength. In order to compare the above mentioned results with other lab-scale studies, a sintering temperature ( $T_{sint}$ ) has been defined as the temperature at which the compression strength of deposits increase above 2 N/mm² and further increases [16]. In Table 5, sintering temperatures for various biomasses and coal are shown. It is seen that straw and grass ashes generally have sintering temperatures within 610-710 °C while wood ashes with higher contents of Si and Ca have higher sintering temperatures, above 780 °C [16].

**Table 5:** Chemical composition and sintering temperatures of various ashes. The sintering temperature is determined by ref [16] based on graphical lab-scale results from the references noted.

Chemical composition of ash [wt%] T <sub>sint</sub> Ref.												
			Chemical composition of ash [wt%]									Ref.
Biomass or coal type		$SiO_2$	CaO	$Al_2O_3$	MgO	$P_2O_5$	$K_2O$	Na <sub>2</sub> O	S	Cl	[°C]	lab-work
Straw	wheat	30.6	7.9	0.5	2.4	4.7	25.3	0.7	2.9	3.7	690	[28]
	wheat	56.3	6.3	0.5	1.4	1.9	12.6	0.2	1.16	2.10	710	[29]
	wheat	34.2	9.1	0.4	2.0	2.1	24.7	0.1	0.92	3.15	660	[29]
Grass	Reed Canary	65.7	2.7		1.8	5.0	4.6		0.56	0.23	960	[29]
	Lucerne	3.3	27.7	0.3	3.1	7.6	28.4	0.7	0.76	4.4	610	[28]
	Reed Canary	72.5	5.6	1.3	1.2	2.5	3.4	0.9	0.8	0.0	690	[28]
Wood	Forrest residue	24.6	25.3	4.3	2.8	3.0	6.9	0.3	1.3	0.1	a	[28]
	Bark	12.2	33.3	1.8	3.7	2.7	7.6	0.5	1.0	0.1	a	[28]
	Olive	44.1	6.7	5.1	3.6	2.1	16	0.3	2.1	-	930	[29]
	Branches and tops	7.3	44.8	1.5	5.8	4.8	11.3	0.8	0.6	-	ь	[29]
	Willow	0.6	28.8	0.1	4.4	10.7	22.5	0.2	2.36	0.18	780	[29]

<sup>&</sup>lt;sup>a</sup>: Compression strength did not increase above 2 N/mm<sup>2</sup> up to a temperature of 1100 °C

By this comparison it is seen that the occurrence of sintering is influenced by both local temperature and chemical composition. The influence of time on sintering is unknown, but expected to have significant influence.

b: Compression strength did not increase above 2 N/mm<sup>2</sup> up to a temperature of 900 °C

# 4 CONCLUSION

Within the last 15 years several measuring campaigns with focus on deposition behavior have been conducted at full-scale power plants firing biomass in Denmark. These measuring campaigns have been reviewed in this work. The focus of the review is the obtained experiences on deposit formation, chemistry and shedding.

A general conclusion is that the flue gas temperature is an important parameter in the deposit behavior of biomass-fired boilers. It is found that increases in the flue gas temperature of both grate and suspension fired boilers leads to increased deposition rates and altered chemical composition of the deposits formed. The increased rate of formation of deposits with increased temperature is considered to be caused by increased melt fractions of fly ash particles and of deposits surfaces. This leads to increased stickiness of the surfaces and thus increased capture efficiency of impacted particles. The impacted particles are mainly large (>10 µm) particles, containing Si and Ca. The increased rate of inertial impaction thus leads to increased contents of these elements in the deposits formed at high flue gas temperatures.

When comparing the two combustion technologies, grate- and suspension-firing, it is found that the rates of deposit formation are comparable, while the chemical composition of the fly ashes are quite different, even for the same type of fuel.

The differences in the entrainment of ash particles from the combustion zone to the flue gas lead to the observed differences in the chemical composition of the fly ashes. For grate fired units, the fly ash is dominated by K and Cl, probably in the form of KCl. This compound has a low melting temperature and will stick to surfaces of particles and deposits. A sticky surface of particles and deposits leads to a high propensity for ash deposition. For suspension fired units, the fly ash is dominated by Si, K and for woody fuels also Ca. The compounds formed from these elements have higher melting temperatures and particles will be less prone to sticking to surfaces upon impaction.

The chemistry of deposits is also varied with variation of firing technology and fuel type. However, some general features of the deposits structure and chemistry are found. The deposits generally have 1-3 layers on the upstream side of the deposition probe; a thin inner layer containing KCl and/or  $K_2SO_4$  and outer layer(s) where fly ash particles (with Si and Ca) may be found, possibly in a molten state, and glued together by KCl or  $K_2SO_4$ .

For straw fired grate units, the contents of Si and Ca in the deposits are limited, and the two elements are predominantly found in the intermediate and outer layers of the deposits. A shift in firing technology from grate firing to suspension firing leads to an increased content of Si and Ca in all layers of the deposits. The deposits chemistry is for suspension fired units found to resemble the fuel ash chemistry. This means that deposits from a woody fuel will have lower Si and Cl contents and higher Ca content as compared to deposits from straw combustion.

The shedding behavior is influenced by both probe surface temperature, flue gas temperature and deposits chemistry. The temperatures of both the probe and the flue gas influence the temperature gradients within the deposits, and thus the degree of sintering. The influence of temperature on the degree of sintering varies with the fuel type. It seems that increased contents of Si and Ca leads to increases in the sintering temperature, and thus to altered shedding behavior. However, the research within this area is limited and based on laboratory scale experiments, so no clear conclusion on the effect of temperature or the chemistry in full-scale applications can be obtained.

Coal ash has been added to woody biomass in suspension firing at Avedøre to possibly limit the deposition behavior of biomass. It is observed that the coal ash addition leads to frequent occurrences of complete shedding events, and the deposit buildup of the biomass ash is thereby minimized. However, as it is planned to substitute all coal combustion with biomass, this solution is only temporarily available.

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