

Effect of Dust Sintering on Fouling of Recovery Boiler Flue Gas Ducting

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Master's thesis

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December 18, 2020

ABSTRAKT

Sodapannor har utvecklats sedan den första Tomlinson-sodapannan uppfanns. Kapaciteten på sodapannor idag är 100 gånger större jämfört med den första sodapannan. Bränslet i sodapannor, svartlut, har även förändrats. För att uppnå större effektivitet i sodapannan tar man bort så mycket vatten som möjligt ur svartlutet. Dessa förändringar leder till förändringar i askan och askans kemi. Nyligen har man noterat nedsmutsning på grund av aska i elektrostatiske utfällare (EP) och vattenvärmare (ECO) i sodapannor. Aska har blivit lättare att fånga upp men svårare att avlägsna.

Målet med arbetet är att uppnå bättre förståelse av askans nya beteende. För att uppnå detta undersöks askans morfologi och egenskaper. Aska kan sintra och orsaka problem i sodapannan. Sintring kan bland annat bero på temperatur, vilket undersöks med sintringstest.

Material som använts till detta arbete är aska från tre sodapannor. I sintringstesten pressades först torkad aska från de tre sodapannorna till piller. Pillren lades sedan i ugn i en viss temperatur och tid. När tiden uppnåtts togs pillren ut ur ugnen och graskades visuellt. Pillren krossades även för att se om de hade sintrats. Piller av sintrad aska visade sig vara svåra att krossa.

Resultatet visar är att ingen sintring sker vid en temperatur på 250 °C och lägre. Sintring sker dock vid en temperatur på 400 °C och 500 °C. Vattenånga ledde inte till sintring vid 250 °C och lägre temperaturer.

Orsaken till askans nya beteende hittades inte. Att sintring inte sker vid 250 °C och lägre temperaturer tyder på att det är något annat fenomen som orsakar nedsmutsning. Inga tydliga skillnader som kan förklara nedsmutsningen hittades i askornas innehåll och smältbeteende. Mängden karbonat i två av askorna var väldigt hög, men eftersom en av pannorna har nedsmutsningsproblem men inte den andra, kan inga slutsatser dras. Den största skillnaden mellan askorna hittades i bilderna från svepelektronmikroskopet (SEM). Aska med det nya beteendet hade agglomererat mera än de andra askorna. Piller gjorda på denna aska krävde även högst tryck för att krossas. För att förklara skillnaderna i SEM bilderna bör mera arbete göras. Att ta reda på var i sodapannan askan undergår agglomeration kan ge svar på askans utseende.

Nyckelord: sodapanna, natrium- och svavelbalans, uppkomst av aska i sodapanna, egenskaper av aska från sodapanna, sintring av aska från sodapannor

ABSTRACT

Recovery boilers today are 100 times the capacity of the original design. The fuel, black liquor, used in recovery boilers has also changed. To improve the efficiency of the boiler, the fuel contains less water. Increased boiler size in combination with increased dry solids in black liquor result in changed dust chemistry in the recovery boiler. Lately, a new type of fouling in boilers has been discovered. Fouling appears mainly in the electrostatic precipitator (EP). Dust is now easier to collect but more difficult to remove. The root cause for fouling has not been confirmed.

The objective of this work is to gain an improved understanding of recovery boiler dust behavior. To achieve this, dust morphology and properties are studied. Dust can sinter in the recovery boiler, making it difficult to remove. Sintering is temperature dependent, which is investigated in this work to evaluate if sintering could explain observations of dust accumulation problems in the EP, boiler generating bank (BGB) and economizer (ECO).

To investigate the dust sintering behavior, experiments were performed. Precipitator dust from three different boilers with different heat loads was pressed into pill-shaped samples. These samples were then placed in an oven. Once the time had been fulfilled, the samples were evacuated from the oven. To determine if sintering had occurred the samples were visually inspected and crushed. The strength needed to crush the samples correlates with the sintering degree.

The result from the dust-sintering experiment was that no sintering occurred at 250 °C and below. Further experiments showed that a temperature of 400 °C was needed for significant dust sintering to take place. Water vapor did not affect sintering of dust.

The reason for the new fouling behavior was not found. Two of the dusts contained extremely high amounts of carbonate, but no correlation between carbonate and sintering could be found. No sintering occurred at 250 °C and below suggesting that EP dust accumulation at these temperatures must be due to another phenomenon or process. The clearest difference in the dusts is in the appearance seen in the pictures taken by the scanning electron microscope (SEM). Dust from the boiler with the new dust behavior is more agglomerated than the other dusts. The crush test showed that the heat-treated pellets made from this dust were also stronger than the other heat-treated pellets. More work is needed to explain the difference in the appearance.

Key words: recovery boiler dust, sodium and sulfur balance, recovery boiler dust formation, recovery boiler dust properties, recovery boiler dust sintering

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PREFACE

This thesis was written for Andritz Oy.

I would like to thank my supervisors Markus Engblom and Keijo Salmenoja for guiding me through the process of writing my thesis. I also want to thank Mikko Hupa and Leena Hupa for their input and help. Finally, I want to thank my family for their support.

Larsmo, December 18, 2020

Jacob Kronqvist

LIST OF SYMBOLS AND ABBREVIATIONS

BB	Boiler bank
BGB	Boiler generating bank
BL	Black liquor
BLS	Black liquor solids
CFD	Computational fluid dynamics
DB	Database
DS	Dry solids
ECO	Economizer
EDXA	Energy-dispersive X-ray spectroscopy analysis
EF	Enrichment factor
EP	Electrostatic precipitator
FMT, T_0	First melting temperature
HHRR	Hearth heat release rate
HHV	Higher heating value
HSM	Hot stage microscopy
ISP	Intermediate-sized particulate
LEFR	Laminar entrained flow reactor
LHV	Lower heating value
MCR	Maximum continuous rating
SEM	Scanning electron microscope
SH	Superheater

1 INTRODUCTION

Most recovery boilers today are Thomlinson-type boilers and the initial design is 90 years old. In recent years, recovery boilers have increased in size (Salmenoja, 2019).

Burning black liquor releases dust. Traditionally, research in recovery boiler dust has been involving the melting properties of dust. Molten dust can cause corrosion on heat transfer elements. The development of recovery boilers can be split into three time periods. Earlier problems were associated to sulfur dioxide (SO_2), and the amount of carbonate (CO_3) was low. In the 90's the amount of SO_2 was reduced, black liquor dry solids increased, and the furnace temperature increased. Carbonate was still low. Recently, SO_2 has been eliminated, black liquor dry solids are even higher and furnace temperatures are higher. The amount of carbonate is also higher. Recently, a new type of fouling has also been recognized. Samuelsson (2018) describes changes in the dust chemistry. Dust is now easier to collect but more difficult to remove in the electrostatic precipitators (EP). Dust deposits are also found in new places, for example, at the EP inlet screen. The reason for these problems is not fully understood. This has also been confirmed by the boiler manufacturers. This new type of fouling seems to be related to high furnace temperatures or hearth heat release rate (HHRR). High furnace temperatures are related to high amount of carbonate in dust, but carbonate does not explain the reason for the problem completely.

Sintering could cause hard deposits of dust in the EP. The dust can sinter either in the EP or in-flight before the EP. In this work, dust from three boilers is studied. One of the boilers is experiencing this fouling problem. To study sintering after deposition as the cause of problems, sintering tests are conducted. To quantify the degree of sintering, a crush test is also conducted on the heat-treated samples. The dust is also analyzed by scanning electron microscope (SEM) for similarities and differences in dust morphology. The objective of this work is to shed some light on the observed new behavior of the dust and its relation to dust morphology and properties. This could provide information to help combat the problem in real boilers.

2 BACKGROUND AND THEORY

2.1 Recovery boiler process

A recovery boiler burns black liquor to heat water into steam. Steam is then led to a turbine which converts the kinetic energy of the steam into power. These are Thomlinson-type boilers, and the original design is 90 years old (Adams, et al., 1997). The heat released from the combustion heats the water into steam. The place where combustion occurs is called the furnace. From the furnace the hot gases flow through the flue gas channel. Pipes with water and steam and air are added throughout the flue gas channel to extract the remaining energy. Many parts of the boiler must work for an efficient process. Optimal black liquor combustion and steam production are important (Vakkilainen, 2005).

2.1.1 Basic principles of recovery boilers

According to the first law of thermodynamics, energy cannot be destroyed or created. This law applies to boilers, the energy released from the combustion of fuels must exit the boiler. The second law of thermodynamics states that energy cannot be converted to another form without increasing entropy. Converting the kinetic energy of steam to mechanical energy and then electrical energy occurs with some losses (Vakkilainen, 2005).

Extracting as much energy from the combustion as possible is performed in many stages and many parts in a boiler. In Figure 1, the main parts of the boiler are shown. The furnace is where the actual combustion of black liquor occurs. Black liquor is provided through the burners. Since the furnace is hot, black liquor ignites. For combustion to occur, oxygen is needed. Air is provided through air ports. In the boiler in Figure 1, three air levels are available. Depending on the configuration some boilers may contain fewer or more air levels.

Since black liquor is not flammable at ambient temperatures, a start-up burner is also a crucial part of a boiler. The process of combusting black liquor releases gases and particles. These end up in the flue gases and in the smelt at the bottom of the furnace. Smelt is a molten mixture of the salts released when burning black liquor. The smelt flows out of the boiler into the dissolving tank through smelt spouts. Flue gases are cooled down by transferring energy to the water and steam in heat exchangers. Flue gases are filtered in the EP. Gaseous compounds condense, forming dust when the temperature is lowered and is collected in the hoppers. From the hoppers the dust is transported with conveyor belts to the mixing tank (Vakkilainen, 2005).

To capture the heat generated by combustion, water is heated in various parts of the boiler. The water provided to the boiler is stored in the feedwater tank. In the economizer (ECO) the water is first heated. After ECO the water runs down the sides of the boiler in downcomers. Steam will be generated in the boiler walls and BGB. Steam, which is less dense than water, will end up in the steam drum. The steam drum separates steam and water. The steam from the steam drum flows to the superheater (SH). After the superheater, steam can be supplied to turbines (Vakkilainen, 2005).

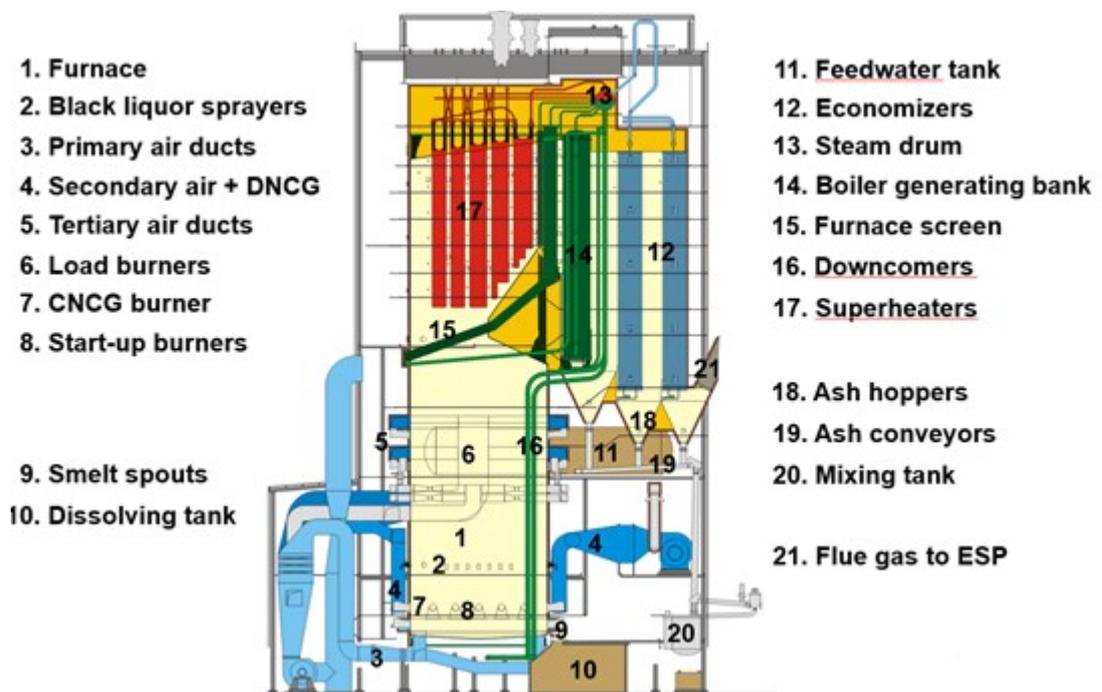


Figure 1: Main parts of a kraft recovery boiler (Salmenoja, 2016)

2.1.2 Combustion of black liquor

The fuel used in recovery boilers is black liquor. Black liquor is sprayed into the furnace, forming droplets. Black liquor consists of the remains of wood after pulping and the chemicals used in pulping. Potassium (K) and chloride (Cl) originate from wood. Sodium (Na) and sulfur (S) originate from chemicals. The chemicals used in pulping are sodium hydroxide (NaOH) and sodium sulfide (Na₂S). Water in the fuel will be turned into steam and end up in the flue gases. This leads to less energy to the heat exchangers and to the power generator. When water is removed from the fuel prior to combustion the content of dry solids increases. The heat released when combusting black liquor comes from the combustion of organic material originating from the pulp wood. Only considering the energy released when combusting dry solids is called higher heating value (HHV). In lower heating value (LHV), the energy lost to making steam out of the water in the fuel is also considered. Since the furnace is hot, the droplets sprayed into the furnace burn as they travel downwards. Air is also provided in the upper furnace to aid combustion. During the flight of a black liquor droplet, it reacts and releases gases and particles. These later form the dust. Optimally the droplet lands in the char bed where it can react into smelt and be tapped out of the boiler. This recovery of chemicals through various reactions makes the recovery boiler a chemical reactor (Vakkilainen, 2005).

Black liquor thermally degrades at 250–500 °C. Different components in the black liquor degrade at different temperatures and rates. Carbon dioxide (CO₂) is released at 200–300 °C due to breakdown of organics and above 500 °C due to breakdown of carbonates. The thermal breakdown of black liquor is largely determined by lignin and carboxylic acids. Aliphatic hydroxy acids release mostly volatiles whereas lignin releases solid residue (Alén, Rytönen & McKeough, 1995).

Na, S, K and Cl determine the condition of the boiler. Black liquor contains varying amounts of these, as can be seen in Table 1. Some sodium and sulfur are in circulation which is called dead load. According to Hupa (2007), around 10% of sodium is in circulation. The condition of the boiler is also determined by the lower furnace and the char bed (Hupa, 2007).

Table 1: Ultimate analysis of black liquor (Ek, Gellerstedt & Henriksson, 2009)

Element	Amount (wt%)	Organic Material	Amount (wt%)
Oxygen	33–38		
Hydrogen	3–5	Hydroxy acid	
Carbon	34–39	Lignin	29–45
Sodium	17–25	Extractives	25–35
Potassium	0.1–2	Acetic acid	~5
Sulfur	3–7	Formic acid	3–5
Chloride	0.2–2	Methanol	~3
Nitrogen	0.05–0.2		~1

2.1.3 Steam production

In order to produce steam, water must be heated. In a recovery boiler water and steam are heated in many locations. Water for the recovery boiler is provided from the feedwater tank. The economizer is where the water is heated before being turned into steam. Heating the water increases the efficiency of the boiler. The superheaters superheat the steam, making sure the steam is dry. Thus, all the water provided into the turbine is in gaseous form. Liquid water in turbines can damage the blades. The temperature of the gas after the furnace can be as high as 1300 °C. (Vakkilainen, 2005).

Heat transfer can occur in three different ways: convection, conduction and radiation. The main form of heat transfer that is occurring in the furnace is radiation. After the furnace, the flue gas still contains heat energy to be transferred into the steam. This is done by convection in the superheaters. The heat from the flue gas is transferred into the metal tubes which transfer the heat to the steam. Convection works best if the air flow and surface area of the heat exchanger is large. The pipes in the flue gas channel are placed so that the heat transfer is as large as possible. Flue gases pass the pipes and transfer heat through convection, in contrary to, the furnace where the pipes are at the wall and transfer heat through radiation. Superheaters, BGB and ECO transfer heat through convection. Turbulent flow of the flue gas ensures that as much heat is transferred as possible. Along the flue gas channel, the temperature decreases as more heat is transferred from the flue gas. If for some reason the heat is not transferred well enough, the temperature in some parts of the flue gas channel may become too high. For example, the economizer where heat from the flue gas is transferred into the water. If the water is heated enough it turns into steam. If the economizer is not designed to handle higher pressures due to boiling, a leak may form. Steam production is not only important for production of electricity but also for the operation of the boiler (Vakkilainen, 2005).

2.2 Dust formation

The dust formed in a black liquor recovery boiler can be classified by formation mechanism or size distribution. Formation of dust is influenced by furnace conditions, black liquor composition and operation practices (Vakkilainen, 2005).

2.2.1 Mechanism

Fume is mostly sub-micron particles that are released from the char bed and in-flight burning of black liquor. Carryover particles are black liquor droplets carried from the furnace via the flue gases. Fragments ejected in the last burning stage of black liquor droplets are called ejecta. Fume is formed when alkali vapors react with flue gas or condense. First, nucleation creates a particle onto which condensation can occur. Supersaturation enable vaporized alkali metals to condense on the particle. Fume can also form by agglomeration, that is, particles colliding and sticking to each other. Almost all dust in the boiler is fume and almost all dust collected in the EP is fume (Vakkilainen, 2005).

Most of the fume is released from in-flight burning. When black liquor is sprayed into the boiler the droplets stay airborne during part of the burning process. Most of the droplets fall to the char bed and continue burning. Cutting off the flow of black liquor into the boiler would cause the in-flight burning to stop. However, the char bed would continue to burn. In an experiment documented by Tamminen et al. (2002), the flow of black liquor was cut off and the dust release was measured during the cut off. All other parameters of the boiler remained unchanged and the fuel was replaced with oil. As can be seen in Figure 2, the dust release decreased by 90% during cut off. This indicates that most of the dust release is due to in-flight burning of black liquor. Before this experiment, it was thought that most of the dust was released from the char bed (Kochesfahani, et al., 2000). The remaining fume is due to vaporization from the char bed (Hupa, 2004).

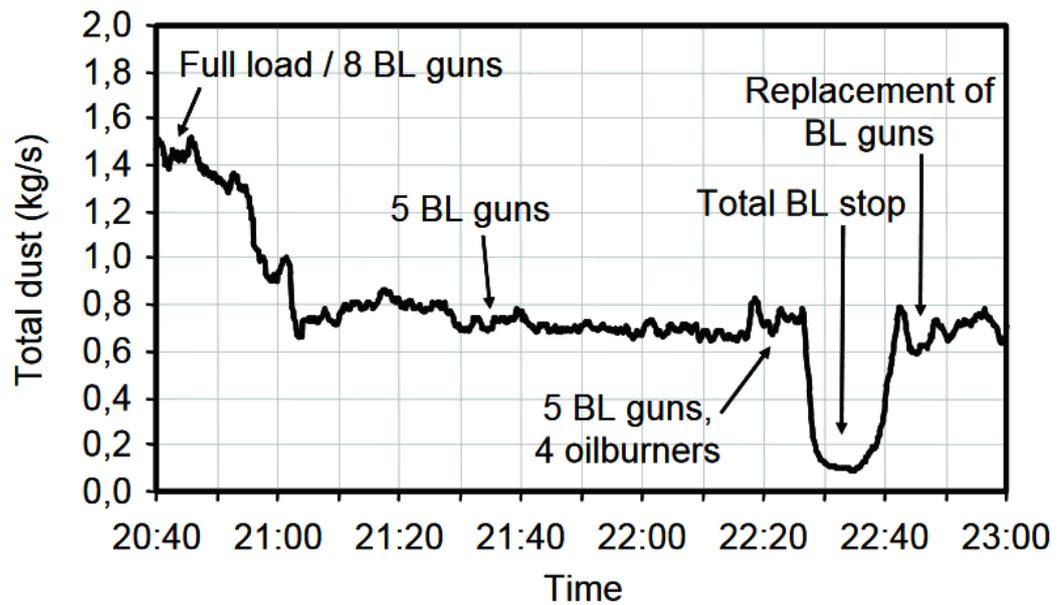


Figure 2: Dust flow in flue gases during an interruption of liquor firing. Measurements made using a continuous dust measuring system (Tamminen, et al., 2002).

Carryover can be divided into two groups, either burnt or unburnt. Unburnt particles cause black deposits due to unburnt carbon. Burnt particles cause pink or red deposits due to sulfidation. Carbon, potassium and chlorine content of carryover is low (Vakkilainen, 2005).

According to Kochesfahani et al. (2000), the formation mechanism of intermediate-sized particles (ISP) is not completely known. The composition of ISP and char bed is similar. This is expected because the temperature in the boiler quickly decreases to 750 °C and the residence time is low, which leads to the particle not fully oxidizing. The intermediate particles are classified according to their formation mechanism (Kochesfahani, et al., 2000):

- Agglomerates from fume
- Soot-blowing irregular particles
- Porous spheres from residue
- Dense spheres
- Mineral impurities

Physical ejection of particles can occur during black liquor and char combustion. ISP can also be released from char bed (Vakkilainen, 2005).

A summary of the release mechanisms of dust in a black liquor recovery boiler can be seen in Figure 3. The burning of black liquor is started when enough heat is transferred to the black liquor droplet. In the drying stage, water is vaporized, and ejecta can be formed. In the next stage of burning, devolatilization, volatiles are released from the droplet. This can cause the droplet to swell and, ejecta and fume to form. Ejecta can continue burning and release fume or become entrained to form carryover. Whole black liquor droplets can also become entrained and cause carryover. Various reactions in the flue gas occur in the char burning stage thus releasing fume. In the last stage, smelt oxidation occurs, releasing sodium and gases, which contribute to fume (Vakkilainen, 2005).

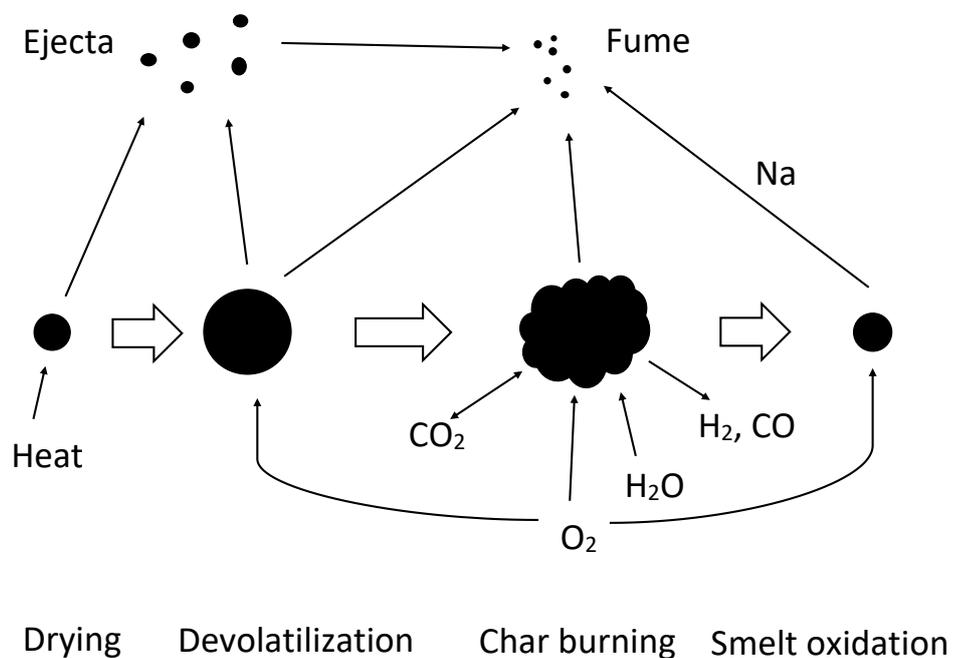


Figure 3: The four stages of black liquor burning, modified from original picture (Hupa, Solin & Hyöty, 1987).

2.2.2 Influence of parameters

Depending on the operation of the boiler either more sodium sulfate (Na_2SO_4) or more sodium carbonate (Na_2CO_3) will be formed in dust (Hupa, 2007). This is often referred to as sulfidity. In a high sulfidity (1.5) process, too much sulfur is present. This implies that some compounds that contain sulfur will remain unreacted. Earlier, recovery boilers have been running a high sulfidity process. In both a low and high sulfidity process hydrogen sulfide (H_2S) and NaOH is released when burning black liquor. In a high sulfidity process more H_2S is released as compared to a low sulfidity process. H_2S then reacts to SO_2 . SO_2 and NaOH then partly reacts to form Na_2SO_4 in a high sulfidity process, whereas almost all SO_2 reacts to form Na_2SO_4 in a low sulfidity process. The flue gas in a high sulfidity process will contain mostly H_2S , SO_2 , sodium bisulfate (NaHSO_4), Na_2SO_4 and Na_2CO_3 . The formation of these can be seen in the upper part of Figure 4. Most of the sulfur compounds react with sodium in a low sulfidity (0.8) process. The remaining NaOH will react with CO_2 . Thus, the flue gas in a low sulfidity process, will contain mostly H_2S , Na_2SO_4 and Na_2CO_3 . The formation of these can be seen in the lower part of Figure 4. In recent years the recovery boiler process has been moving towards a low sulfidity process (Hupa, 2007).

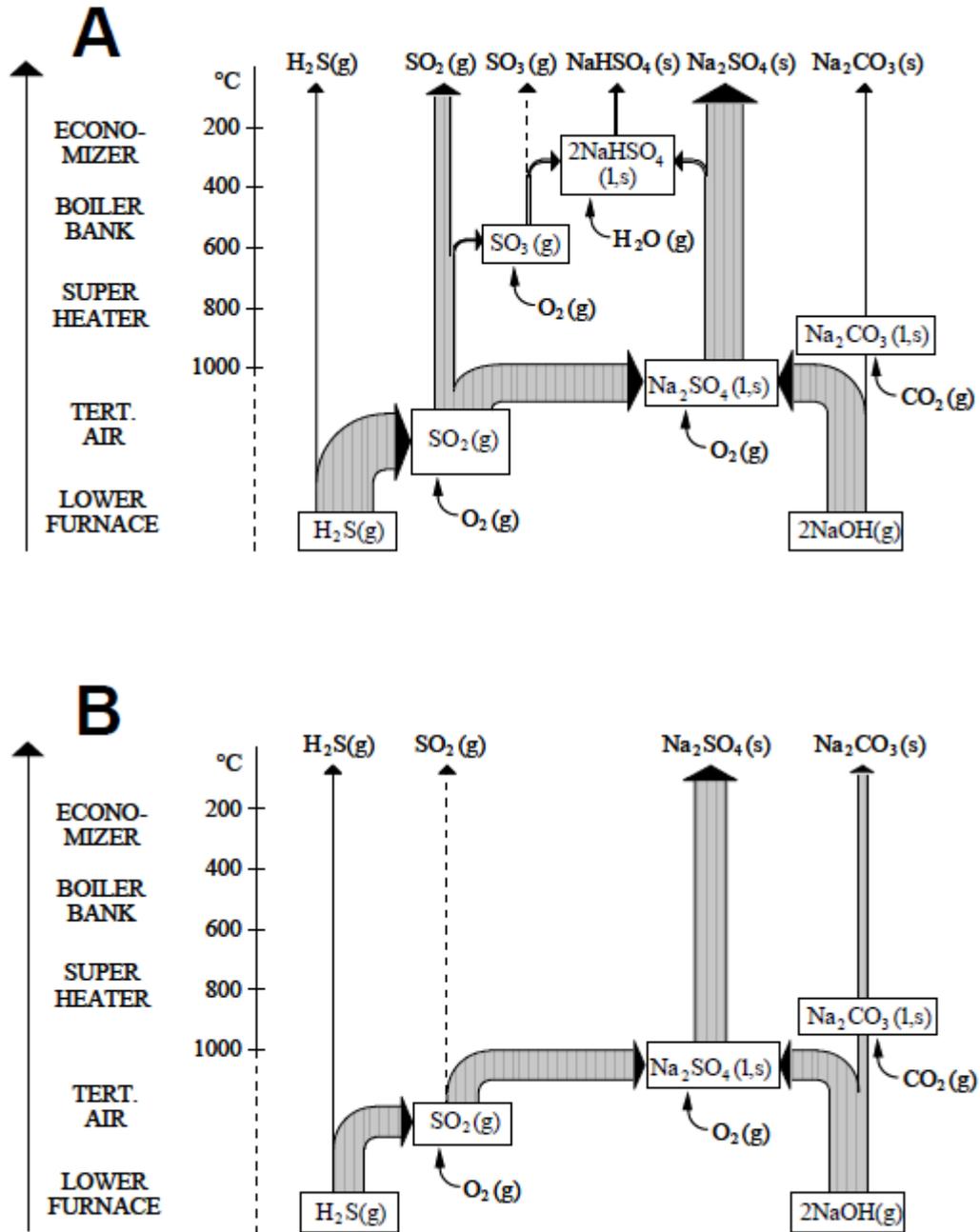


Figure 4: Reactions of sulfur and sodium in recovery furnace and flue gases. A) (upper) Molar ratio in flue gases: $S/\text{Na}_2=1.5$ (Cool bed, high sulfidity). B) (lower) Molar ratio in flue gases: $S/\text{Na}_2=0.8$ (Hot bed, low sulfidity) (Adams, et al., 1997).

The S/Na₂ ratio of dust is temperature dependent (Hupa, 2007). Higher temperatures release more Na₂CO₃ and lower temperatures release more Na₂SO₄. This dependence can be seen in Figure 5. The values for this Figure are obtained from boilers of different types and sizes. Similar findings were obtained by Mikkanen et al. (1999). According to Hupa (2007), it is generally known that lower operating temperature causes higher sulfur concentration in flue gas. Temperature influences sulfur release and is inversely proportional. Increasing lower furnace temperature by 100 °C leads to 25% lower sulfur release. Some sources find high sulfur release at high temperatures in droplet burning tests. However, measuring sulfur release in droplet burning tests provides a higher result than in actual boilers. The heating rate of black liquor droplets also affects the sulfur release (Tamminen, 2002). Vaporization of Na₂S increases with temperature, which leads to it oxidizing. Higher temperatures release more ISP. Temperature also increases chloride release, but not as much as sodium release increases with temperature (Vakkilainen, 2005). Figure 5 shows the equilibrium of the reactions at different temperatures and how the observed values are three times as high. However, the observed values do not respond as quickly to the temperature as the equilibrium (Hupa, 2007).

By measuring the pH of the dust, the ratio of Na₂CO₃ and Na₂SO₄ formed can be checked. Na₂CO₃ acts as a buffer and Na₂SO₄ is neutral. Typically, the pH of dust is 10–11. High alkalinity could indicate increased vaporization of sodium which indicates an increased amount of dust in the EP (Hupa, 2007).

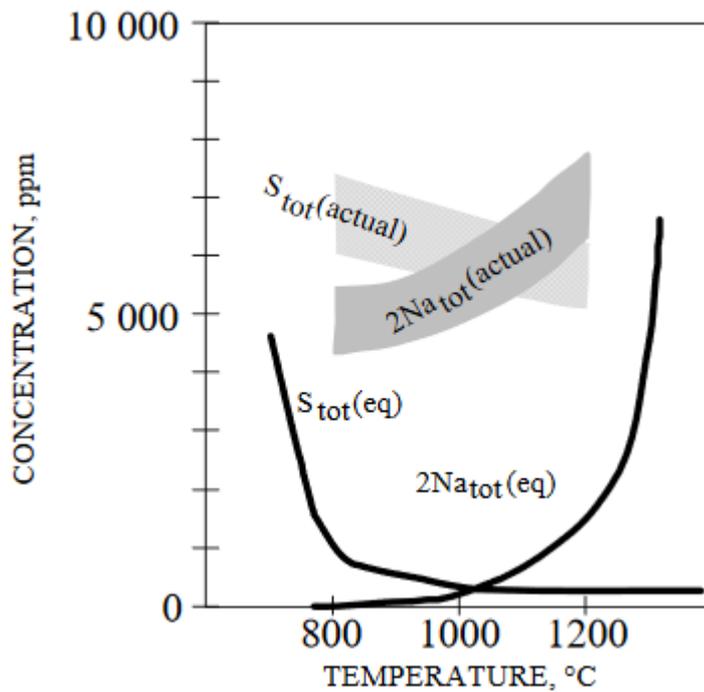


Figure 5: Sulfur and sodium release in recovery furnaces as function of temperature. Equilibrium values and typical actual boiler data (Hupa, 2007).

According to Hupa (2007), it is also generally known that increasing the operating temperature of the boiler will increase dust load. The amount of fume increasing with temperature can be seen in real boilers. One way to increase the temperature in a boiler is to increase the thermal energy input. Thus, the thermal energy input per floor area increases. Thermal energy input per floor area is called hearth heat release rate (HHRR) (Vakkilainen, 2005).

The condition of the boiler can also be affected by varying dry solids content of black liquor. Higher content of dry solids in black liquor indicates that more water has been removed from black liquor. With less water to absorb energy in combustion, the temperature in the furnace will increase. This also leads to increased power generation. The S/Na₂ ratio in dust is affected by the dry solids. The content of dry solids in black liquor, increases the temperature of the furnace and increases the sodium release, which leads to more sodium than sulfur available for reaction. More sodium carbonate will be formed thus decreasing the S/Na₂ ratio of dust. More dust will also be formed as can be seen in Figure 6. Black liquor dry solids content does not seem to affect the release of sulfur. However, at high dry solids almost no SO₂ is formed in the boiler (Tamminen, 2002).

Tamminen et al. (2002) found that the amount of dust is related to the load, exponentially after 80% load. Fume stands for 6–8 wt% of black liquor solids (BLS). The composition of dust is not correlated to load (Tamminen, et al., 2002). In Figure 2, the amount of dust is decreased when the number of firing black liquor guns is brought down from eight to five.

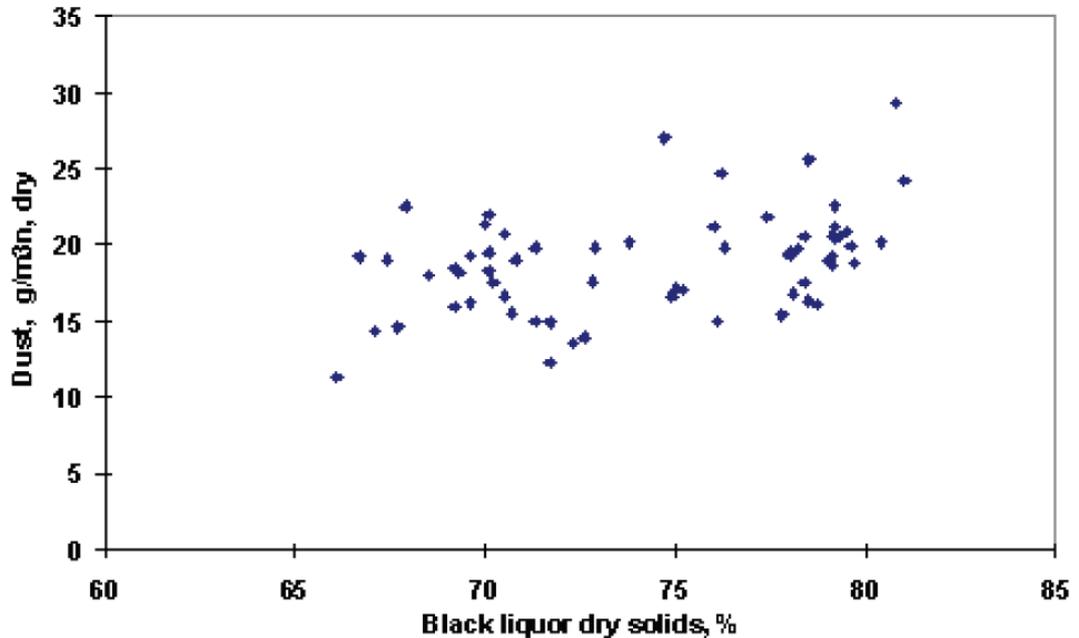


Figure 6: Measured EP dust concentration from recovery boilers (Vakkilainen, 2005).

Release of chloride is linearly correlated with chloride content in black liquor. Adding potassium chloride (KCl) to black liquor in an entrained flow reactor increases the release of chloride (Khalaj, Kuhn & Tran, 2006). The same correlation can also be seen in real boilers (Tamminen, 2002).

2.2.3 Composition

According to Vakkilainen (2005), the composition of dust is mostly a combination of these salts: sodium chloride (NaCl), KCl, Na₂CO₃, potassium carbonate (K₂CO₃), Na₂SO₄ and potassium sulfate (K₂SO₄). In Table 2, the average composition of recovery boiler dust, based on many measurements from many boilers, can be seen (Adams, et al., 1997).

Table 2: Composition of recovery boiler dust (Adams, et al., 1997)

Na (wt%)	K (wt%)	S (wt%)	Cl (wt%)	CO ₃ (wt%)
32.1	0.9	20.1	2.5	3.5

The most common reactions in a recovery boiler can be seen in Figure 7. Mikkanen (2000) states that Na_2CO_3 is unlikely to be released from black liquor due to temperature, causing decomposition. Alén, Rytönen & McKeough (1995), found that Na_2CO_3 decomposes at around 500 °C. However, Na_2CO_3 plays a role in char oxidation (Vakkilainen, 2005). Of the total amount in black liquor, 6–9% Na, 11–15% K and 25–35% Cl is released as dust (Tamminen, 2002).

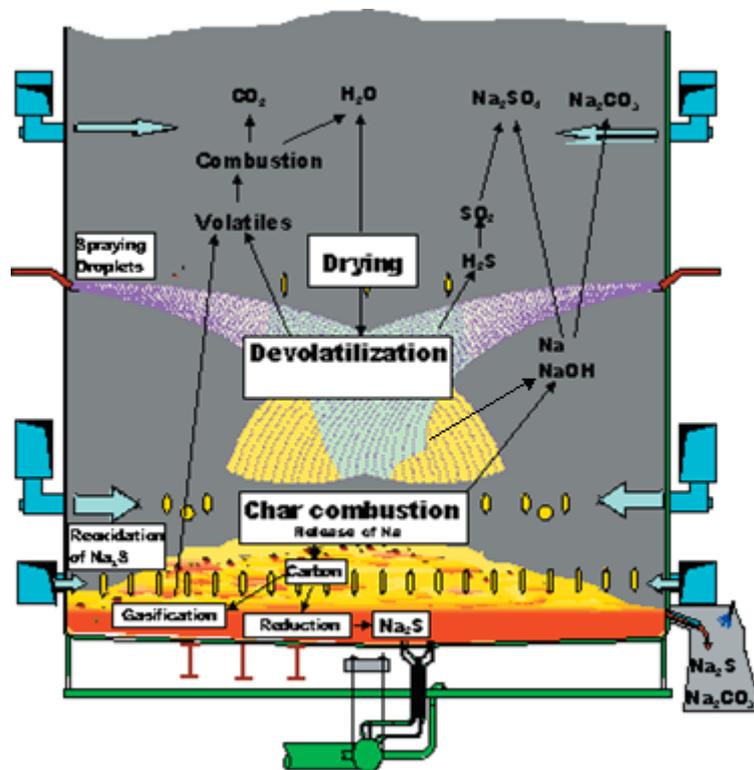
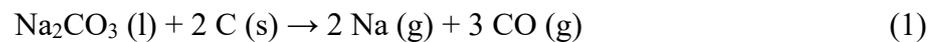


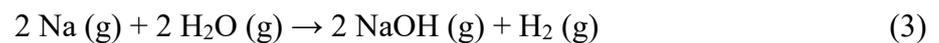
Figure 7: Some of the reactions in the lower furnace (Vakkilainen, 2005).

All EP dust comes from compounds made from reactions involving vaporized sodium. Dust is mostly fume. Fume composition can be determined by release rates of Na, K, S and Cl. In general, fume will be enriched in compounds with higher volatility such as K and Cl. The higher the temperature, the more important Na becomes due to volatilization. In an experiment conducted by Kochesfahani, Tran & Jones (2000), ejecta was low in Cl and S but rich in CO_3 .

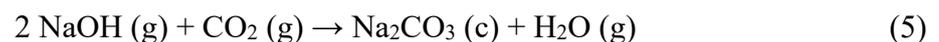
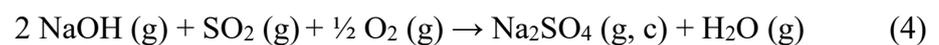
10–30% of sodium released in dust originate from the char bed (Vakkilainen, 2005). Ejecta could account for some of the sodium release when burning black liquor. In experiments performed by Kochesfahani, Tran & Jones (2000), pyrolysis of large black liquor droplets showed release of sodium while small droplets did not show release of sodium. However, Saw et al. (2010), found that sodium release increases with decreasing droplet size. Vaporization of potassium and sodium is minimal during devolatilization but occurs during char burning. Char burning occurring in-flight will form different compounds because of exposure to flue gases as compared to char burning in char bed. In-flight char burning accounts for 90% of sodium released in dust. According to Tamminen (2002), sodium is released from black liquor because of thermal breakdown. The release process can be seen in Reaction (1) and (2). Carbon in these reactions is supplied from black liquor char.



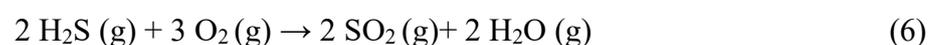
Sodium vapor is not likely to exist in furnace. Sodium is more likely present as NaOH, Na₂CO₃ and NaCl. Gaseous sodium released will react with water vapor released from drying or burning black liquor, which can be seen in Reaction (3) (Vakkilainen, 2005).



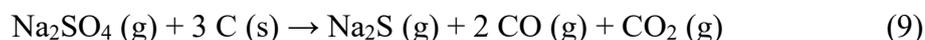
NaOH can then react with SO₂ in Reaction (4) or CO₂ in Reaction (5), depending on the availability of SO₂. If more sulfur is released, more Na₂SO₄ will be formed, and if more sodium is released, more Na₂CO₃ will be formed. This relationship is discussed in Chapter 2.2.2. These reactions occur in the upper part of the furnace and partly in the superheater (Hupa, 2007).



10–40% of the sulfur in black liquor is released in flue gas. According to Hupa (2007), sulfur is vaporized from black liquor in the form of H₂S and carbonyl sulfide (COS). In Reaction (6) H₂S is reacted with oxygen (O₂). The SO₂ produced can then react with NaOH in Reaction (4).



Some of the smelt in the bed can evaporate and oxidize, as summarized in Reaction (7). The Na produced can then react with water vapor in Reaction (3). According to Grace, Cameron & Clay (1985), smelt on the surface of black liquor droplets create a cycle of reactions to oxidize char as summarized in Reaction (8) and (9).



Sulfur and sodium react with each other in many reactions in the boiler. A lot of research around sulfur has been done due to the restriction on sulfur emissions. Recovery boilers operating at a sufficiently high temperature will not have problems with SO₂ emissions. Most sulfur is bound to inorganics in black liquor. Organically bound sulfur ranges from 30–40%. 20–40% of the total sulfur in black liquor is released as flue gases. However, the release decreases with furnace temperature (Adams, et al., 1997). Some is released as H₂S which can be seen in Reaction (10) (Tamminen, 2002).



Released chloride is mostly NaCl, which is vaporized. The release is affected by vapor pressure and the exact species is not known. The possibilities are Cl, Cl₂ and NaCl. Some chloride reacts quickly to form hydrogen chloride (HCl). Some NaCl remains unreacted.

In laminar entrained flow reactor (LEFR) as much as 60% of total chloride in black liquor can be released, but vapor pressures do not play a role in LEFR so results may not reflect on real boilers (Kochesfahani, Tran & Jones, 2000).

Potassium in black liquor originates from wood and is 3–5% of the amount of sodium. Potassium and sodium are similar in the fact that they form similar compounds that behave similarly. The release of potassium correlates with the release of sodium but not the release of chloride. A significant amount of potassium is released by vaporization of KCl (Vakkilainen, 2005).

The main carbon consuming reaction in a boiler is the reduction of char. Char does not directly react with oxygen but reacts through intermediary compounds. In an optimal boiler, sodium is tapped out as smelt at the bottom of the furnace. Sodium and sulfur will react with each other if the conditions are right. In the char bed, where conditions optimally are reductive, a smelt is formed and tapped out of the reactor. Conversely, Samuelsson et al. (2014), found that improved air supply in boilers caused more Na_2CO_3 to be formed through oxidizing conditions. For the smelt not to be oxidized, the air ratio in the char bed needs to be below 0.8. Char is a good reducer, which helps the process. From the total amount of sulfur injected into the boiler, 90% is usually tapped out as Na_2S . (Hupa, 2007).

Enrichment factor (EF), refers to how the ratio of a species relative to other species has changed, in this case between dust and black liquor. For example, the enrichment factor for potassium is usually 1–2.5, which means that the ratio of potassium compared to other species increases by 1–2.5 in dust as compared to black liquor. The enrichment factor can be calculated using Formula 1. Enrichment of potassium decreases with carbonate content since higher temperature in the furnace releases more sodium and thus, carbonate. Since potassium is more volatile than sodium it will be enriched in EP dust. The enrichment factor for chloride is usually between 0.3 to 6. Chloride salts have higher vapor pressures than other components in the flue gas and will thus, be enriched in EP dust. Chloride enrichment decreases with decreasing temperature and thus also dry solids content. Increased dry solids content of black liquor increase EP dust due to enrichment of chloride and potassium. Enrichment factors show trends not absolute values (Vakkilainen, 2010).

$$EF = \frac{\left(\frac{n_A}{n_K+n_{Na}}\right)_{dust}}{\left(\frac{n_A}{n_K+n_{Na}}\right)_{BL}} \quad (1)$$

where

n is the molar amount (mol)

A is a chemical species

2.3 Dust properties

Recovery boiler dust has different properties depending on formation mechanism. Dust, which is a mixture of salts, also has a different melting behavior compared to, for example, a metal. Another relevant property for dust is resistivity, which determines how easy it is to filter out from the flue gases (Vakkilainen, 2005).

2.3.1 Particle size

Carryover becomes entrained in the flue gas and has a size of 100 μm –3 mm with an average size distribution of one mm. Fume has a size of 0.1–1.3 μm . Ejecta, particles ejected from the bed, have a size of 1–100 μm , and the amount released is unknown. In Figure 8 carryover and ISP can be seen, fume which is much smaller cannot be seen.

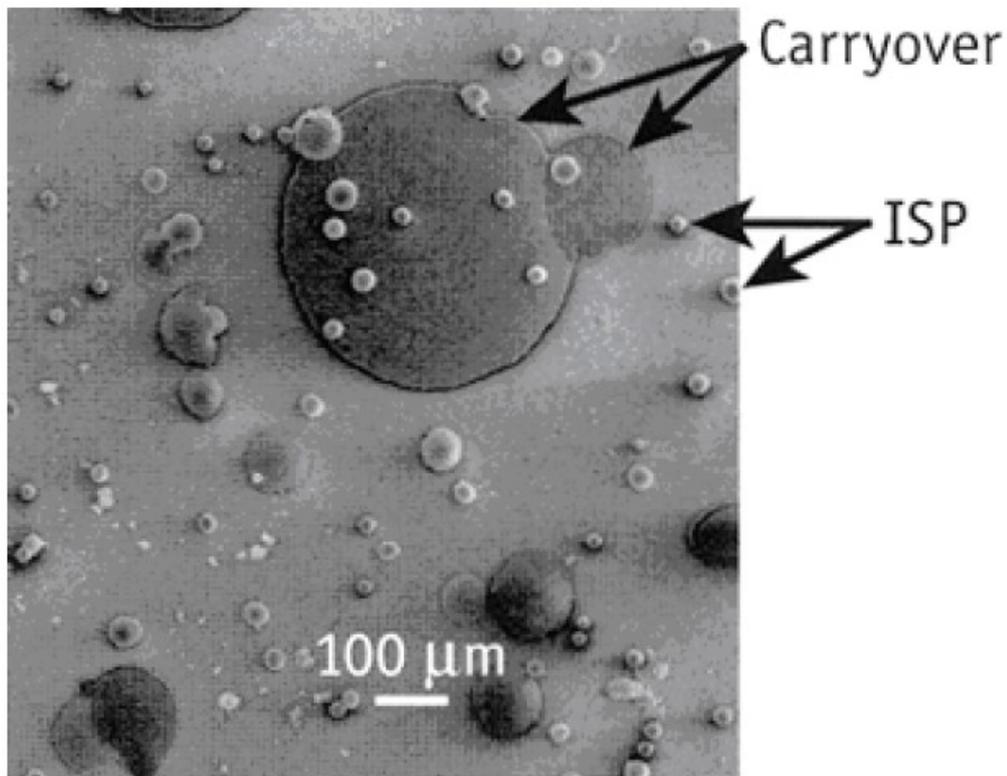


Figure 8: Intermediate size particles (Kochesfahani, et al., 2000)

In the experiment conducted by Kochesfahani, Tran & Jones (2000), the collected particles were bimodal, 1–100 μm , ejecta and sub-micron sized fume, each representing their own data. Ejecta formed from char bed was spherical and light brown while fume particles were white and sintered. Spherical particles suggest melting and then solidification. The experiment may not be representative of a real boiler. The average size of the particles collected in this experiment was 20 μm . Physical separation of particles was not possible. According to Tran (2007), particles collected just before EP are coarser in texture due to soot blowing. Soot blowing frees deposits from heat transfer surfaces which drop down in the boiler.

Dust particle size increases with dry solids content of black liquor due to increased agglomeration. Higher dry solids content leads to higher furnace temperature which increases sodium release. Dust formation is also proportional to firing rate. In the experiment documented by Tamminen et al. (2002), the particle size decreased with decreased load. This is due to lower concentration of dust which leads to less agglomeration. Particles stuck to heat transfer surfaces can also form agglomerates with fume. These particles can grow to 20–30 μm (Vakkilainen, 2005).

ISP size distribution varies according to release mechanism:

- Agglomerates from fume: $0.3 \pm 0.7 \mu\text{m}$
- Soot blowing irregular particles: $30 \pm 250 \mu\text{m}$
- Porous spheres from residue: $5 \pm 100 \mu\text{m}$
- Dense spheres: $5 \pm 250 \mu\text{m}$
- Mineral impurities: $3 \pm 40 \mu\text{m}$

Notice the high variability of soot-blowing particles.

2.3.2 Melting behavior

When dust starts to melt, problems appear in the boiler. Dust which usually contains a mixture of salts has a more complex melting behavior than a single salt. Instead of one melting point, mixtures involve a melting range in which the mixture is partly molten and partly solid, depending on composition of the mixture. The melting range can span several 100 °C. The first point when melting of mixtures of salts occurs is called T_0 or first melting temperature (FMT). This point can be lower than the melting points of the individual salts in the mixture. The point where the mixture is completely molten is called T_{100} (liquidus). These mixtures also involve a sticky range when it is more likely to stick to surfaces in a boiler. The sticky range is between 15% and 70% of the mixture being molten, T_{15} and T_{70} . At T_{15} enough melt is available to glue it to surfaces and at T_{70} enough melt is available in the deposit to flow off the surface. The latter is also called slagging. When the deposit starts flowing off the surface, it has reached steady-state thickness. That signifies that the surface temperature of the deposit has reached T_{70} . This implies that the deposit thickness remains unchanged over time. The concept of steady-state deposit thickness is illustrated in Figure 9. Dust is not sticky but may cause deposits when the temperature in the flue gas is lower than FMT (Wessel, et al., 2004).

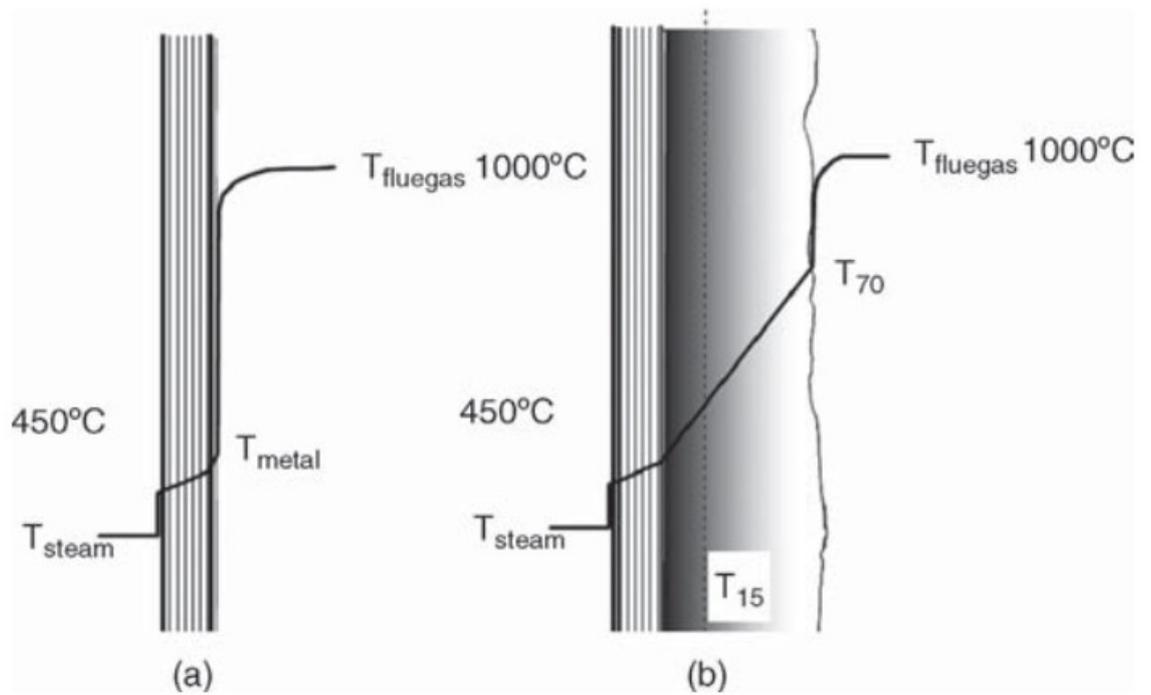


Figure 9: Temperature profile across a superheater tube wall: (a) clean tube and (b) tube covered with a deposit grown to its steady state thickness (Zevenhoven, Yrjäs & Hupa, 2010).

In tests conducted by Frederick & Vakkilainen (2003), morphology, composition and sintering characteristics of alkali metal salts from a boiler were determined. They found two types of particles using an air-cooled probe, fume and ISP. The composition of these particles was mainly Na_2SO_4 but contained potassium, chloride and carbonate too. FMT depends on the composition of the particle, carbonate and potassium lower the FMT. In Figure 10, the effect of carbonate at different potassium levels and temperatures can be seen. If chloride is present, FMT will also be low. In Figure 11, the effect of chloride and potassium on the sticky range of dust can be seen. Chloride affects FMT greatly until 5–6 mol% $\text{Cl}/(\text{Na}+\text{K})$ is reached. Without these FMT can be as high as 810 °C (Duhamel, Tran & Frederick, 2004).

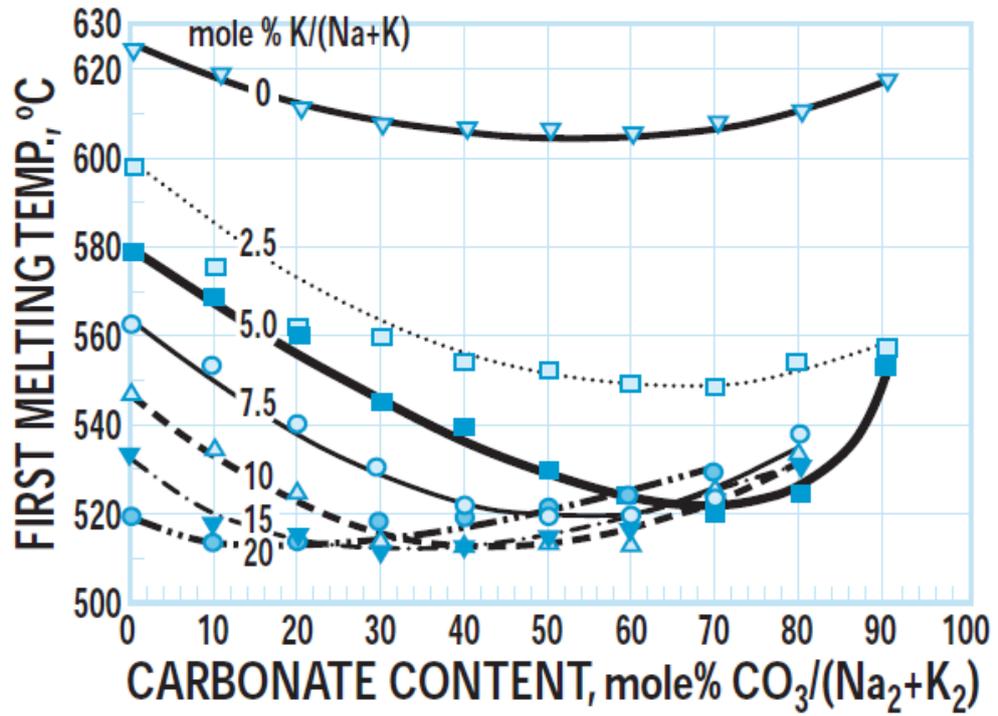


Figure 10: Effect of carbonate on the FMT of synthetic deposits at different potassium levels [chloride content = 5 mole% Cl/(Na+K)] (Tran, et al., 1999).

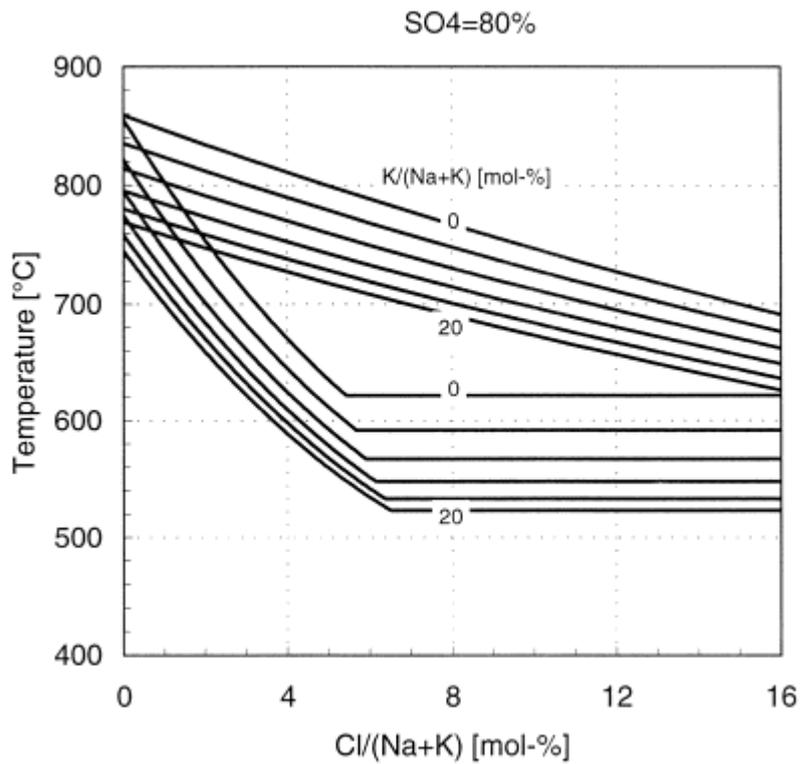


Figure 11: Calculated diagram showing the effect of chloride and potassium on the sticky temperature and flow temperature of salt mixtures containing sulfate and carbonate (Backman, Enestam & Zevenhoven, 1998).

2.3.3 Sintering tendency

When sintering occurs, particles fuse together. As opposed to melting, sintering does not displace the space between the particles. This indicates that sintering can occur with a minimal change to the appearance, whereas melting permanently deforms the material. On a microscopic level, connections between particles appear when sintering occurs. These connections are called necks. This leads to strengthening of the material. Further sintering is called neck growth, where the connections become larger. Sintering can occur in significantly lower temperatures than melting. Lab tests suggest that sintering can occur rapidly (Vakkilainen, 2005).

Number of contacts between particles determine sintering degree. For sintering chains to develop particles must be connected to two other particles. For the rigidity of the deposit to increase, particles must be connected to more than four other particles. Thickening of nodes and branches can occur with little densification. Once contact is achieved between particles, densification can occur. The rate of sintering depends on FMT which in turn depends on potassium and carbonate content (Vakkilainen, 2005).

Dust in some boilers can sinter. Depending on location in the boiler, different particles deposit. This is partly due to different temperatures in the boiler. Techakijkajorn, Frederick & Tran (1999) studied the effect of temperature on sintering. The locations used in the tests conducted by Frederick & Vakkilainen (2003) can be seen in Figure 12. In location A, at the first two superheaters, partially sintered fume, irregular particles from soot blowing and spheres with dendritic coating of fume can be found. Soot blowing will release more large particles which can emerge in deposits. At the other locations deposit is mostly fume. Location also influences structure of the deposit. This is partly due to sintering increasing with temperature. At location B, at the last two superheaters, more deposits with dendritic structure can be found, 4–5 μm nodes or grains with 1–2 μm branches. In the center of the deposit, larger nodes, 5–8 μm , that have had more time to sinter can be found. The inner surface of the deposit had even larger nodes.

At location C, at the first boiler bank (BB), sintered agglomerates of fume were detected. Individual fume particles were evident with small necks. At location D, at the second boiler bank, soft and crumbly deposits could be found. Location D is the most relevant for this work. The study by Techakijjajorn, Frederick & Tran (1999), however, does not include the EP, where the temperature is even lower and sintering should be slower. The temperature at location D was estimated to be below 400 °C. The deposit showed no neck thickening and was only slightly sintered. The composition of dust also varies depending on location. In a similar test conducted by Tavares et al. (1996), composition was determined, and the results were similar. Carbonate and sulfate varied, chloride varied greatly with a factor of two, potassium and sodium did not vary much.

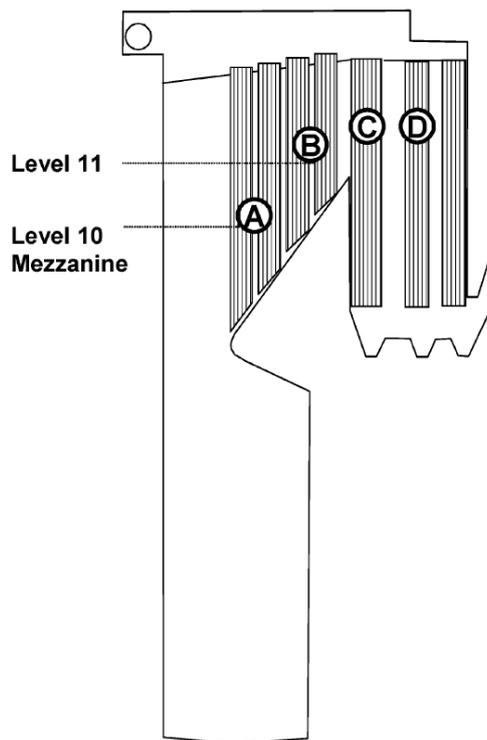


Figure 12: Diagram of the recovery boiler at the Metsä Botnia Group pulp mill in Joutseno, Finland, showing the locations (A-D) where deposition probes were inserted (Frederick & Vakkilainen, 2003).

2.4 Dust related issues in recovery boilers

Combustion of black liquor releases vaporized inorganic chemicals and char fragments. These become entrained in the flue gas and deposit on heat transfer surfaces which could lead to problems. Most problems in black liquor recovery boilers is due to lower furnace release of carryover and fume. Ejecta can contribute to fouling of superheaters and generating bank in the boiler. Smaller particles such as fume find their way to the EP.

2.4.1 Fouling and plugging

Optimal heat transfer is important for running a recovery boiler. Burning any fuel will cause dust to form. Dust may then, through different processes, end up on the heat exchanger surfaces in the boiler. The heat transfer through dust is lower than the heat transfer through clean tubes. Dust, therefore, acts as an isolating layer on the tubes. Dust may form on heat exchanger surfaces due to thermophoresis, condensation or impaction (Adams, et al., 1997). Strength of the deposit is an important property and depends on melting and sintering. Dust can plug the superheater, boiler generating banks and economizers. These deposits can be removed by soot blowing. If not removed the deposits can harden through sintering or thermal densification (Frederick & Vakkilainen, 2003).

Heat transfer is determined by area of the heat exchanger and temperature difference. Deposits caused by fouling, lower the temperature difference. The cause for fouling is often simplified. To determine the cause of fouling the location in the boiler, changes in the process and properties of black liquor, is important. Relevant properties in black liquor are sulfidity, chloride content and potassium content. For example, increase in dry solids content decrease economizer fouling and an improved air system decreases superheater fouling. Fouling is different in different boilers. It could be measured differently and there could be upset correlated to fouling. Generally, to combat fouling decreased flue gas temperature and soot blowing is efficient (Vakkilainen, 2005).

Deposition is different depending on particle size, small particles may deposit due to thermophoresis, larger particles due to impaction, vapors and gas due to condensation. Thermophoresis is proportional to temperature gradient, particle diameter and particle concentration. Vapors and gases can condense on particles in the boundary layer or the heat transfer surface. For tiny particles, smaller than 0.1 μm , molecular diffusion and Brownian motion is relevant. Thermophoresis affects particles in the size range of 0.2–1 μm and is directly proportional to the temperature gradient between hot flue gas and colder heat transfer surface. However, Baxter et al. (2004), found that thermophoresis does not explain the deposition in an experimental boiler. In the experiments the structure of the deposit was string-like. They also found that gas and particles were able to permeate the deposit which could improve collection efficiency. Leppänen (2015), suggests that using the temperature difference instead of temperature gradient in calculations can provide incomplete results. She states that thermophoresis is the dominant effect when it comes to deposition of fume on heat transfer surfaces. Inertial impaction affects particles larger than 20 μm and capture efficiency is determined by inertia. Turbulent eddy impaction occurs when turbulent boundary layers supply enough momentum to large particles causing them to impact with heat transfer surface. Rate of deposition is determined by particle size distribution, temperature difference, heat transfer surface composition and dust concentration in flue gas.

When talking about fouling, the growth rate of the deposit is important. This can be tricky to measure without shutting down the boiler, but methods exist. Measuring can be performed by temperature, pressure or visually. More specifically pressure loss or temperature of flue gas or steam. Pressure loss is however, also determined by boiler load. When the gas flow area decreases due to deposits, the velocity increases, thus, causing a pressure drop. If the flue gas fan cannot keep up with the pressure drop, boiler load must be lowered. Computational fluid dynamics (CFD) is a powerful tool as well and can help picture changes in carryover. Deposition on superheater is caused by inertial impaction and fume. Low flue gas velocity also causes good collection efficiency, which increases the amount of deposit (Vakkilainen, 2005).

Deposits in superheater lower heat transfer and thus, steam temperature, which can lead to a higher temperature in the boiler generating bank. Deposits on the boiler bank are caused by low dust melting point, increased chloride, high temperatures and fast sintering. Deposition in the economizer is caused by low dust pH, which is not a problem if at least 10% carbonate is present. Carbonate increases the pH (Vakkilainen, 2005). At higher dry solids content more carbonate is released. Predicting deposition is difficult with temperature because of the amount of needed measuring points. Pressure loss is commonly used today but can only be used for predicting deposition in boiler bank and economizer. Deposition on the superheaters is predicted with steam temperature which is directly proportional to heat flow. Attemperating, or how much water is needed to keep constant steam temperature is also a good predictor (Vakkilainen, 2005).

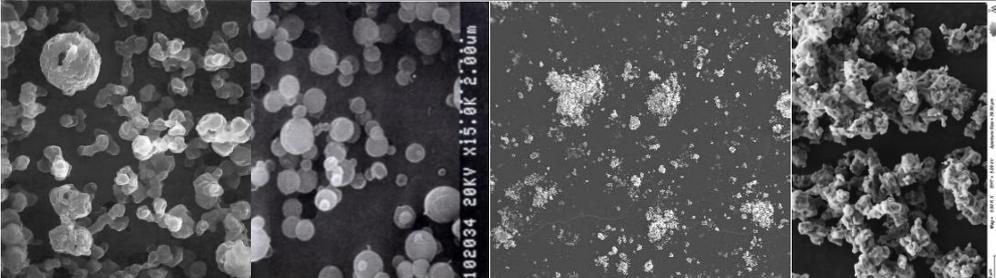
Frederick et al. (2004), was able to predict BB fouling with FMT, chloride content and BB temperature. In another study, by Frederick et al. (2004), FMT was determined to be the most important factor for fouling. FMT decreases over time because of decreasing carbonate content. Carbonates react with SO_2 and oxygen to form sulfates. This process is called sulfation. Carbonate is released as CO_2 . In combination with sintering, sulfation can produce hard deposits. If soot blowing is performed in proper intervals the deposit will not have enough time to harden (Frederick & Vakkilainen, 2003).

Fouling can also occur in the EP. Samuelsson (1999), found that deposits continue reacting in EP, which may lead to electric shielding, thus, problems. She also found that agglomeration of dust occurs when the boiler is running on a medium load, but not when running on a high load. Chemical reactions including adsorption of water lead to sintering. Na_2SO_4 can react to form sodium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$) and NaHSO_4 . If SO_2 is present in flue gas over an extended period, a hard deposit will form. If conditions are reducing Na_2S could be formed, which is extremely hygroscopic and will form sticky deposits. NaOH may be present which is hygroscopic damp and sticky. NaOH reacts with CO_2 to form Na_2CO_3 . NaCl is polarized and will form chains in deposit which produces fluffy dust.

In recent years changes in the recovery boiler process have changed the fouling behavior in a recovery boiler. Parts of the boiler, for example, the inlet screen to the EP, now have fouling problems. In Table 3, changes in the chemistry of EP dust can be seen. Carbonate has increased significantly while sulfur is decreasing. In the SEM pictures differences can also be seen. EP dust is agglomerated in 2020 whereas earlier it was not (Samuelsson, 2018).

Table 3: Changes in the recovery boiler process and dust properties from 1980-2012 * (Samuelsson, 2018), **2020 data from this work

(wt%)	~1980*	~1995*	2012*	2020**
Na	29	28.2	31	32.6
K	3.1	5.2	2	5.2
S	64.7	59.6	44.9	40.6
Cl	3.1	2.9	1	2
CO ₃	0.1	1.1	12.9	19.5
ds	63	73	76	80
SO ₂	high	low	0	0
Dust (g/Nm ³) dry	5-12	15-25	37.5	25-30



Sulfation can also contribute to sintering, however, only at high SO₂ concentrations, approximately 10000 ppm. In the tests (Frederick & Vakkilainen, 2003), the SO₂ concentration was 1–3 ppm. Tran, et. al (2000) found that most of the carbonate to sulfate reaction occurs in the superheater. Gases that contain sulfur cause the most problems in the flue gas channel (Hupa, 2007).

2.4.2 Corrosion

Corrosion in a recovery boiler can be split into two categories, water side and fire side. Fire side corrosion can be split into high temperature and low temperature. Water side corrosion is caused by impurities in feed water. High temperature corrosion occurs in superheater, and low temperature corrosion in economizer and air pre-heater. Low temperature corrosion can be caused by acidic compounds. Molten alkali metals cause most corrosion in the gas side of the boiler, but gases can also cause corrosion if the conditions are reducing. Corrosion rates differ between areas in the boiler. Usually steel tubes contain a protective oxide layer. Depending on how easily this oxide layer is penetrated, corrosion will occur.

Chromium, nickel and manganese in steel form oxide layers that are difficult to penetrate. Iron(II,III) oxide (Fe_3O_4) is more protective than iron(III) oxide (Fe_2O_3), which gases can penetrate. Sulfidation can cause corrosion when H_2S reacts with iron, to form iron(II) sulfide (FeS) above $310\text{ }^\circ\text{C}$. Stainless steel resists this type of corrosion up to $480\text{ }^\circ\text{C}$. High temperature corrosion is caused by vanadium, sulfur and alkalis. Thin and molten deposits can be corrosive. Reactions in molten phase are faster than reactions in solid phase. Molten phase can, for example, dissolve corrosion products. Carbon steel corrodes fast, thus a frozen protective layer on top of it, is important. FMT affects corrosion, if it is low enough, the deposit will flow off. Alkali corrosion tends to leave a smooth surface whereas other types of corrosion can form pockets. Chloride is a corrosive element and will react with iron in oxidizing conditions. NaCl , Cl_2 and HCl will react to form iron(II) chloride (FeCl_2). FeCl_2 will form Fe_2O_3 which chloride can penetrate, and then react with iron thus creating a cycle. High carbonate, or high dry solids content in black liquor can counter chloride corrosion as can be seen in Figure 13. Deposit properties and SO_2 affect corrosion rate. Acid sulfate corrosion can occur below $450\text{ }^\circ\text{C}$ and one of the acidic compounds is sodium bisulfate. Dew point corrosion can also occur with sulfur trioxide (SO_3) (Vakkilainen, 2005).

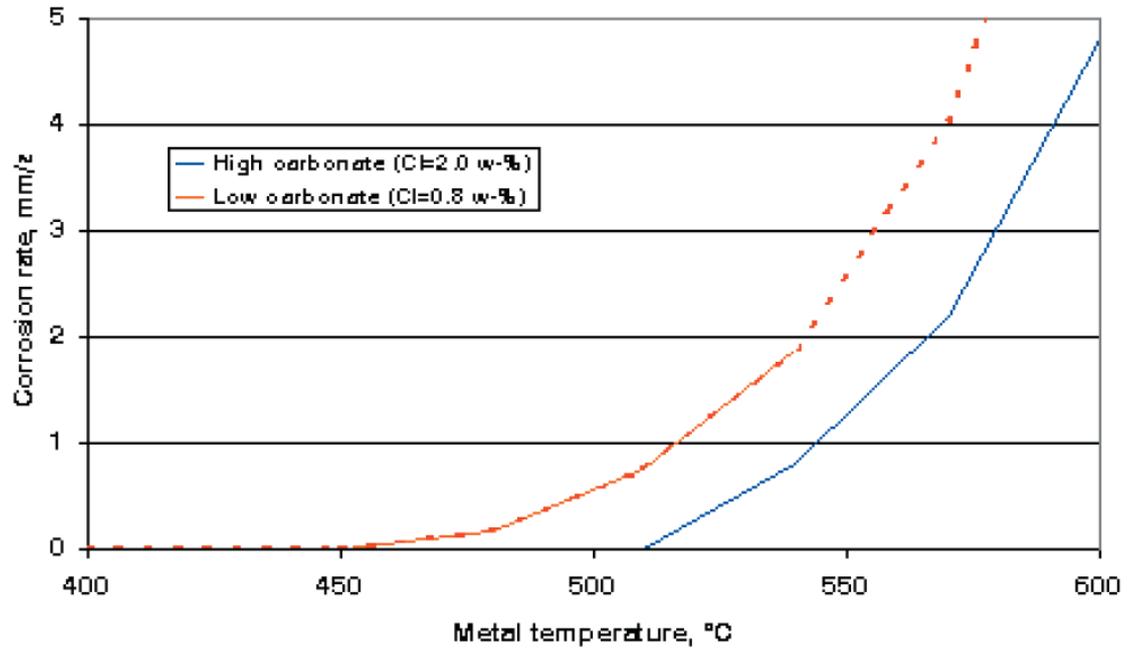


Figure 13: Effect of operating conditions on corrosion rates of superheater tubes from two boilers (Vakkilainen, 2005).

3 MATERIAL AND METHODS

3.1 Analysis of recovery boiler dust by SEM

For this thesis, recovery boiler dust from three different boilers were provided. These dusts were analyzed using various techniques. In Table 4, relevant properties of the boilers, from which the dusts originate, are listed.

Table 4: Comparison of relevant properties from three recovery boilers

RB	ds (%)	Wood	HHV (MJ/kgds)	HHRR (kW/m ²)	CO ₃ (wt%)	Fouling
A	83.8	Hardwood	13.7	3146	30	No
B	78.25	Hardwood	13.77	3897	22	Yes
C	75.8	Softwood	13	2936	7	No

The dust morphology was analyzed using a SEM. The composition of the dusts was analyzed using an EDXA. From the data from the EDXA, the amount of carbonate in the dusts can be calculated, using Formula 2.

$$n = \frac{m}{M} \quad (2)$$

where

n is the molar amount (mol)

m is the mass (g)

M is the molar mass (g/mol)

To calculate the carbonate, stoichiometric balance is assumed, which implies that no material is left when the products are formed, the sum is 100%. The products included in the calculation are: Na₂SO₄, Na₂CO₃, NaCl, K₂SO₄, K₂CO₃ and KCl. Since the measurement of oxygen in the EDXA is inaccurate, it is not used in the calculation. The remaining mass when all products are included is assumed to be oxygen and carbon. All chloride is assumed to form salts, and all sulfur is assumed to be SO₄. When all the sulfur and chloride is consumed for the products, the remaining potassium and sodium is assumed to form carbonates.

To determine the sintering tendency for the dusts, a hot stage microscope (HSM) was used. The basic principle of HSM is a camera which takes pictures, at specific intervals, of a sample which is in an oven. In this case, a picture every 5 °C is taken. The temperature is gradually increased so that changes to the sample can be seen over time in the pictures. For this analysis, the heating rate was 10 °C/min, from room temperature to melting temperature. Melting temperature is considered 20% of original sample height. The temperature at which the picture is taken is also recorded. The height of the sample determines sintering.

1. Sintering point: the first ca 5% decrease in height
2. Maximum shrinkage point: the sample edges still sharp but the sample shows maximum shrinkage
3. Softening point: softening or rounding of the edges; this is also known as minimum base line point
4. Half-sphere point: the sample forms a semi-sphere
5. Flow point: the sample has floated out or fused with the substrate (often around 20% of original height)

In Figure 14, melting of a sample can be seen. The sample is 2 mm in diameter and 3 mm high. The softening point and half-sphere point are not available for the dusts analyzed.

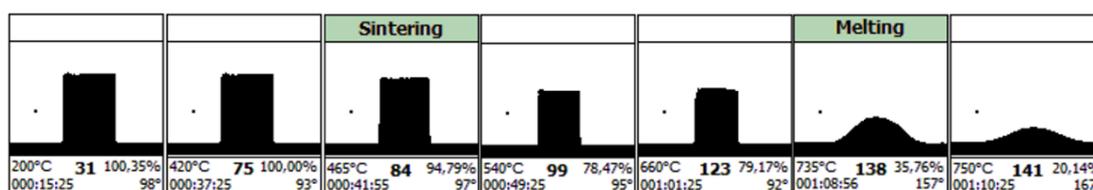


Figure 14: Significant points when sintering RB B dust in HSM

To calculate the melting properties of the dusts FactSage was used. FactSage is a thermochemical database system. For thermodynamic calculation, all species with their quantities for each dust are put in the software. The species and quantities were provided by the EDXA. Quantities were added in moles or grams. The species were added as cations and anions. The data collected after the calculations were amount of melt in grams in the temperature range from 400 °C to 1000 °C. Since the dusts contained varying amounts of CO₃, the total mass of the samples varied. To correct this, the amount of melt was normalized as % instead of grams.

3.2 Sintering tests

For sintering tests, samples were placed in an oven for a time period to ensure that the sample sinters. The oven was pre-heated to the desired temperature and the samples from different boilers were placed in the oven at the same time to eliminate errors, for example, temperature difference. The oven temperature was monitored with a thermocouple. The heating was automatically cut off when the desired temperature was reached and turned back on when the temperature decreased below it. When the desired time was reached, the samples were extracted from the oven and allowed to cool at room temperature.

For pellet manufacturing, an 8 mm die set, and a hydraulic press was used. For pellets sufficiently tall, the die had to be refilled a few times and pressed again. The amount of pressure used had to be high enough for the pellet to stay intact but low enough to prevent layering. The dust used for pellets was dried in a 130 °C oven for 24 hours prior to manufacturing. The pellets were stored in a desiccator prior to sintering. To determine if sintering had occurred, the pellets were inspected visually and crushed. Pellet shrinkage and color change implies that it had sintered. The test matrix can be seen in Table 5.

A crush tester can be used for determining the strength of an object, in this case sintered pellets. Sintered pellets are more difficult to crush. A pellet is placed between the plates of the crush tester and the plates are pushed together at a rate of 1 mm/min. A force sensor records the highest force needed to crush the pellet. For this test, six pellets from every boiler, sintered at 400 and 500 °C, were used, totaling 36 samples. Since the results are measured in force, they can be calculated into pressure by dividing by the area of the pellet.

The original plan was to see if sintering occurred at 150, 200 and 250 °C. This temperature interval corresponds to the temperature interval in which EPs operate. However, in the first three experiments the pellets appeared unchanged after being in the oven at 250 °C for 2, 4 and 24 h. The pellets were soft enough to be crushed between fingers, indicating that no sintering had occurred. The fact that no sintering had occurred at temperatures as high as 250 °C led to skipping the tests at lower temperatures. Instead, sintering at 400 and 500 °C was performed. These temperatures were selected so that sintering would occur according to the sintering curves. According to the HSM analysis and sources, sintering does not occur below 350 °C. At 350 °C sintering occurs slowly. At 400 and 500 °C sintering occurs faster.

Table 5: Matrix of performed tests

Test	Time [h]	Temperature [°C]	Salt	
1	2	250	RB A,B,C	Air
2	4	250	RB A,B,C	Air
3	24	250	RB A,B,C	Air
4	24	250	RB A,B,C	Air + 20 vol% H2O
5	2	400	RB A,B,C	Air
6	2	500	RB A,B,C	Air

4 RESULTS AND DISCUSSION

4.1 Morphology and composition

The composition of the dusts analyzed by EDXA can be seen in Figure 15. Comparing these results a few differences can be seen. The dust in RB C has less potassium and less carbonate. RB A and B are extremely high in carbonate. RB A is high in potassium and RB B is higher in chloride than the other boilers. Dust from RB C represents the typical non-problematic dust. Dust from RB B is problematic but does not stand out when it comes to composition.

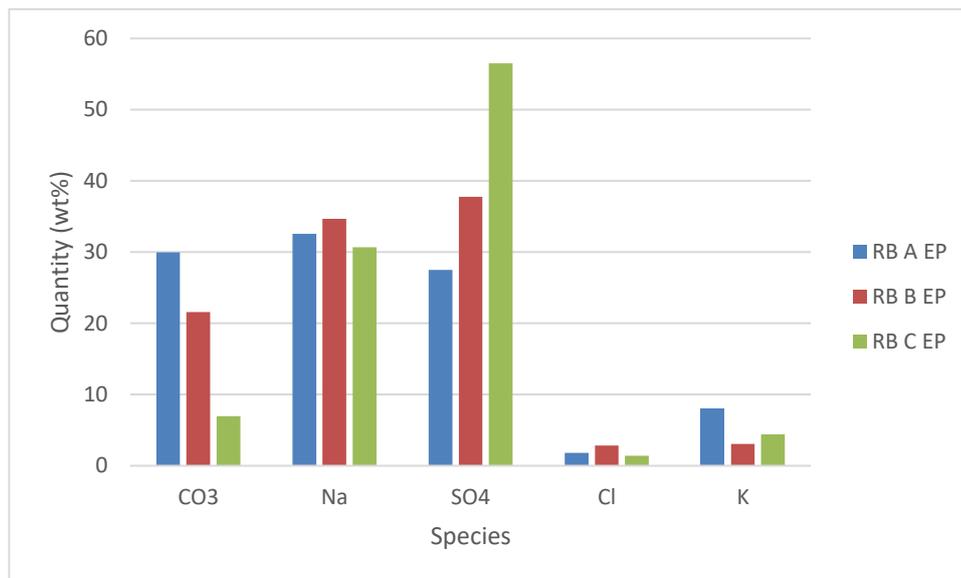


Figure 15: Recovery boiler dust composition from three different recovery boilers using EDXA

The results from calculating the melting properties using FactSage can be seen in Figure 16. Calculated melting temperatures are shown in Table 6. According to Duhamel, Tran & Frederick (2004), sintering increases with chloride and potassium content in EP dust. This could explain the fouling problems in RB B since the EP dust is high in Chloride, however, it is also low in potassium.

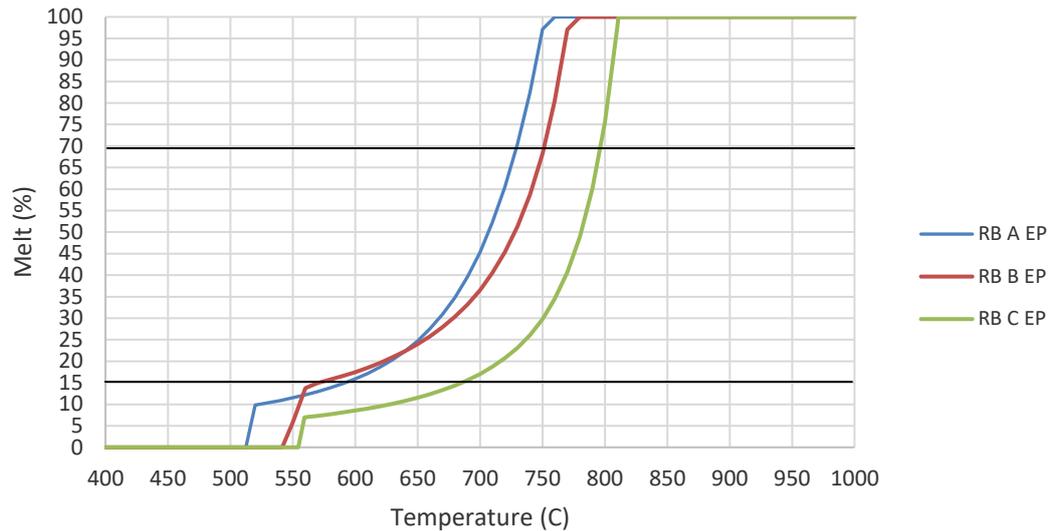


Figure 16: Melting behavior of EP dust from three different boilers

Table 6: Characteristic melting temperatures of EP dust from three different boilers

Dust	T ₀ (°C)	T ₁₅ (°C)	T ₇₀ (°C)	T ₁₀₀ (°C)
RB A	512	585	725	752
RB B	541	575	750	777
RB C	552	680	800	816

The results from FactSage suggest that the dusts involve different melting temperatures. RB B has more chloride than the other boilers, thus, it has the lowest T₁₅. This agrees with the results by Backman, Enestam & Zevenhoven (1998). RB A has the lowest T₀ temperature because the dust contains the most potassium and carbonate, which agrees with the results by Tran, Gonsko & Mao (1999) and Frederick & Vakkilainen (2003). Dust from RB C is the least problematic when it comes to fouling since T₀ and T₁₅ are high. T₁₅ is lower in RB B dust than RB A dust, however, RB A has lower T₇₀ which also makes the dust less problematic. The point where RB A dust melts at higher temperatures than RB B dust (circa 640 °C) can also be seen in Figure 20. The first crossing point between RB A and RB B dust cannot, however, be seen in the other results, this is due to inaccurate calculation below T₁₅. Out of all the melting temperatures, carbonate seems to have the largest effect on T₁₅. The most relevant temperature for ECO and EP is T₀. Since RB B had fouling problems in EP and ECO it should be visible in T₀, however, RB A had the lowest T₀ temperature.

In Figures 17–19, SEM pictures of dust from the EP from recovery boilers A, B and C, can be seen. Differences in appearance can be seen from these figures. Dust from RB A has formed small agglomerates. Dust from RB B has formed large agglomerates. Dust from RB C has also formed agglomerates, but individual particles can still be seen. It is difficult to characterize dust morphology using some sort of measure, but differences can be seen in the SEM images. The difference in appearance can be connected to differences in dust formation in-flight processes and conditions. More work is needed to understand better the differences seen in the SEM images.

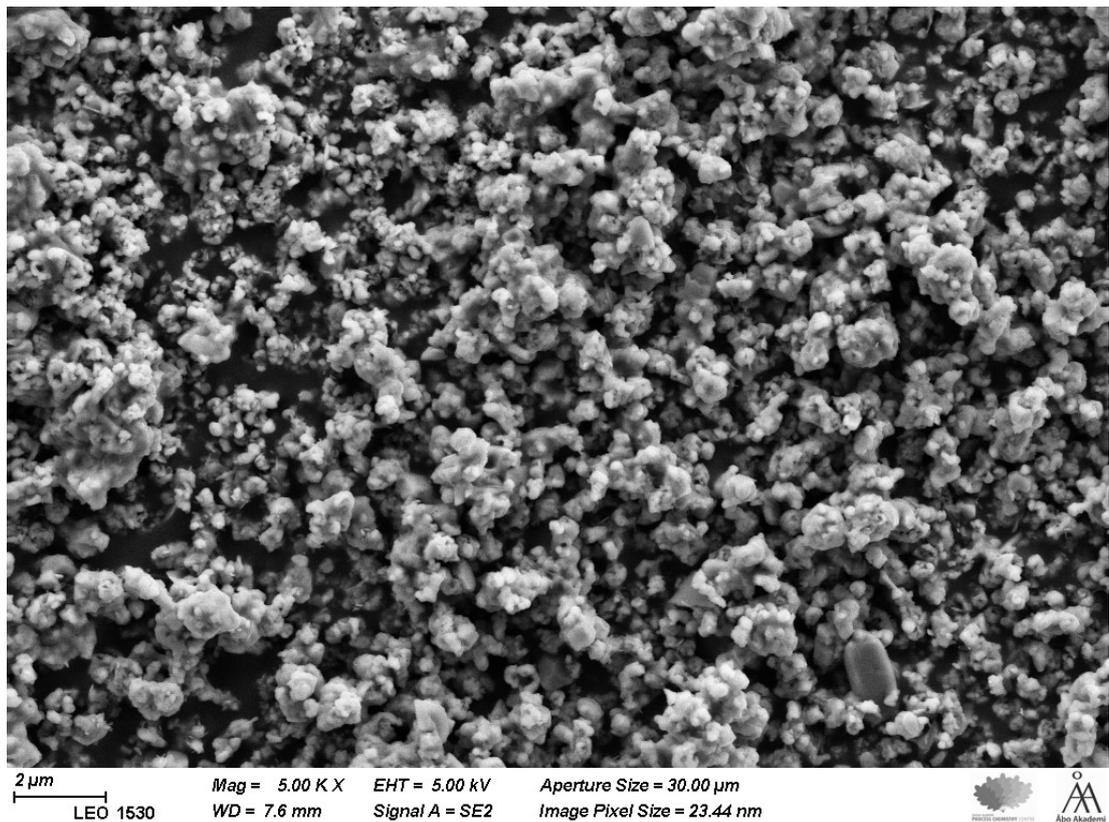


Figure 17: RB A EP dust SEM image, slightly sintered, submicron and irregular particles

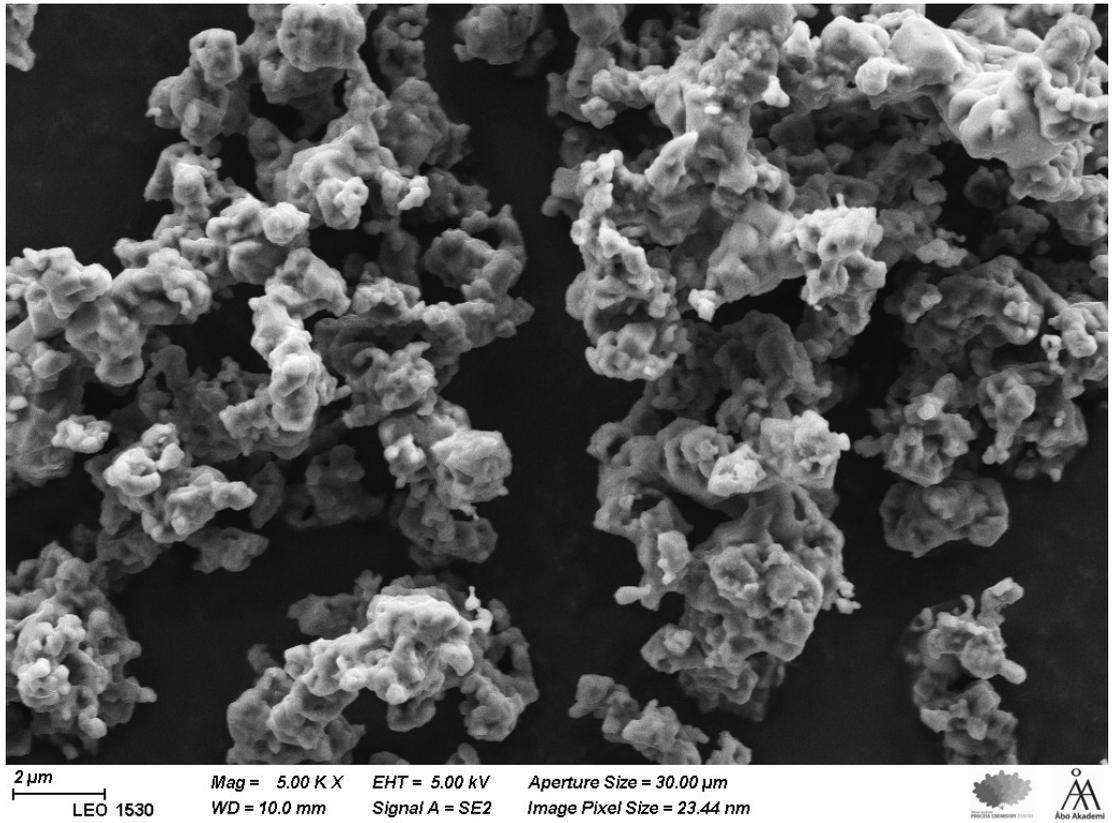


Figure 18: RB B EP dust SEM image, highly sintered agglomerates larger than one micrometer

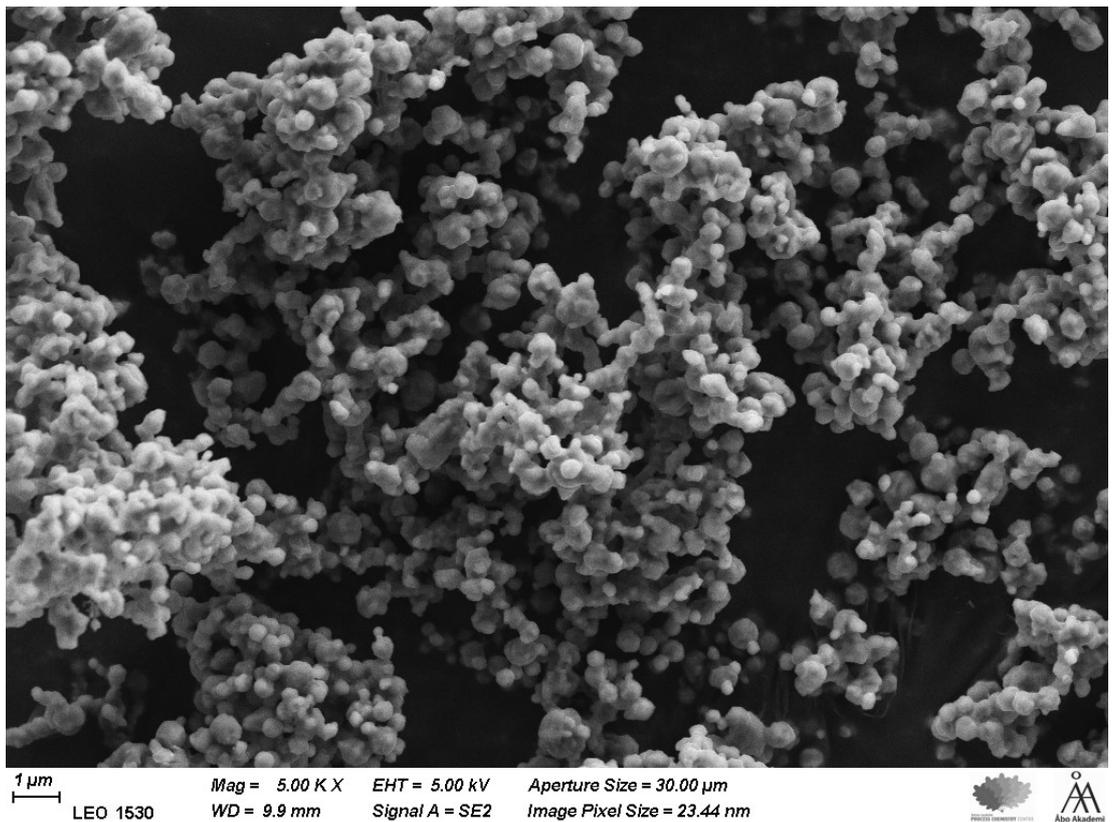


Figure 19: RB C EP dust SEM image, agglomerated but still visibly round, submicron particles

4.2 Sintering behaviour

In the HSM analysis, the dusts did not sinter below 350 °C, which can be seen from the sintering curves in Figure 20. The results from the sintering test show no sintering below 250 °C. Similar results were found by Techakijkajorn, Frederick & Tran (1999). This suggests that sintering in EP is not due to temperature. In a real boiler, other parameters, for example, chemical sintering, that could affect sintering are present. According to the HSM analysis, sintering occurs at 400 °C, which can be confirmed by the sintering tests. According to Duhamel, Tran & Frederick (2004) initial sintering degree can affect sintering. RB B dust is more sintered than the other dusts when looking at the SEM images. RB B dust also sinters later according to the HSM analysis. Pictures of dust pellets sintered at 500 °C also reveals a difference between RB B dust and the others. This could be a symptom of fouling in RB B. Initial sintering does not affect the composition or calculated melting behavior of the dust. They also state that FMT influences sintering, but RB B does not have the lowest FMT. The melting temperatures were compared to the temperatures used for the sintering tests. This confirms that the samples did not melt in the sintering tests and that hardening of the samples was most likely due to sintering.

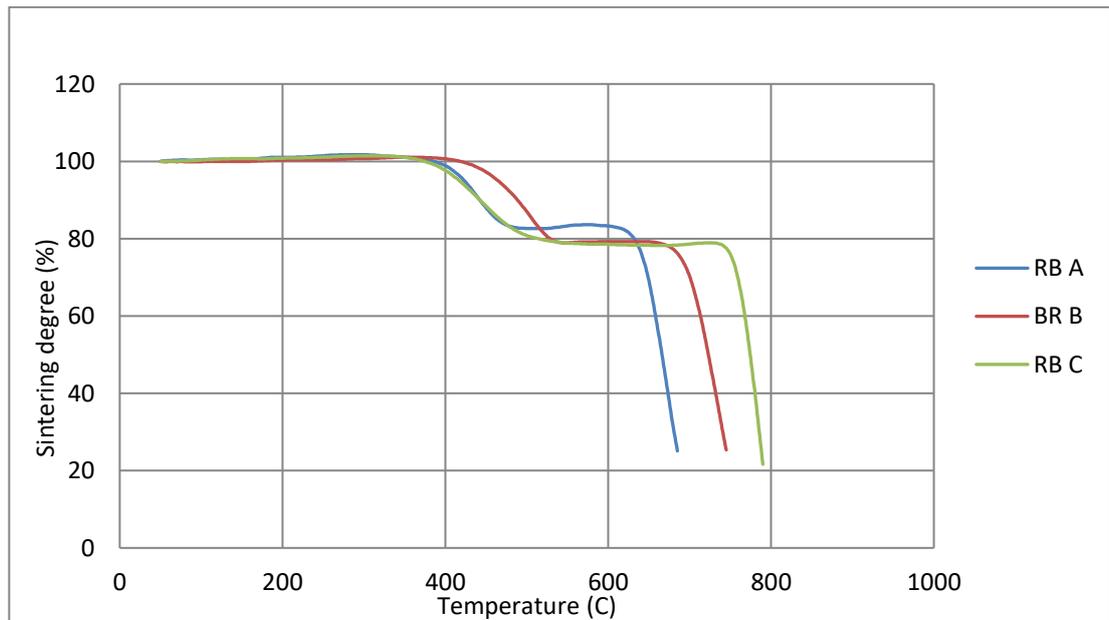
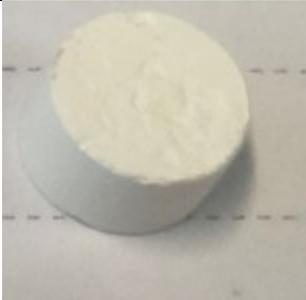


Figure 20: Sintering curves for EP dusts from three different boilers.

In Table 7, the different dust samples after sintering can be seen. The samples to the right in this table are sintered at 500 °C. The samples in the middle are sintered at 400 °C and the samples to the left are sintered at 250 °C. To determine if water vapor, which exists in flue gases of a boiler, affects sintering, a test in a water vapor atmosphere was conducted. However, the pellets remained unchanged and soft enough to be crushed between fingers. No sintering had occurred. The pellets at 400 °C appeared to be smaller in size and were almost impossible to crush between fingers. The pellets sintered at 500 °C were even smaller in size and impossible to crush between fingers.

Table 7: Pictures of dust pellets from RB A,B and C sintered at 250 °C for 24 h, 400 °C for 2 h and 500 °C for 2 h. Pellets sintered at 250 and 400 °C show minimal changes, while pellets sintered at 500 °C vary in appearance. Pictures are in the same scale.

R B	250 °C	400 °C	500 °C
A			
B			
C			

Six samples of dust from each boiler were used for every temperature and time, totaling in 108 samples. Six samples are enough to eliminate errors due to, for example, a poor sample. Visual inspection is good for detecting changes in color and size, but to really guarantee that a sample is sintered, it should be analyzed in a SEM. Using a hydraulic press to make pellets may make the dust stronger, however, Techakijkajorn, Frederick & Tran (1999) found that sintered pellets had the same strength even though the initial density, before sintering, of the pellet was different. The height of the pellets could make a difference, however, the difference in strength between a sintered pellet and a non-sintered pellet is so large that the height does not make a difference (Techakijkajorn, Frederick & Tran, 1999).

In Figure 21, the results from the crush test can be seen. The pellets sintered at 250 °C were too soft to be measured by the crush tester. However, pellets sintered at 400 and 500 °C were hard enough for numerical values to be obtained. Since these are below the melting temperature of the dusts, the only reason for the increased strength can be sintering. The pellets were all manufactured in the same way, which leaves out strength due to pressing. Comparing these results to the SEM images, the boiler (RB B) with the strongest dust also has the largest agglomerates.

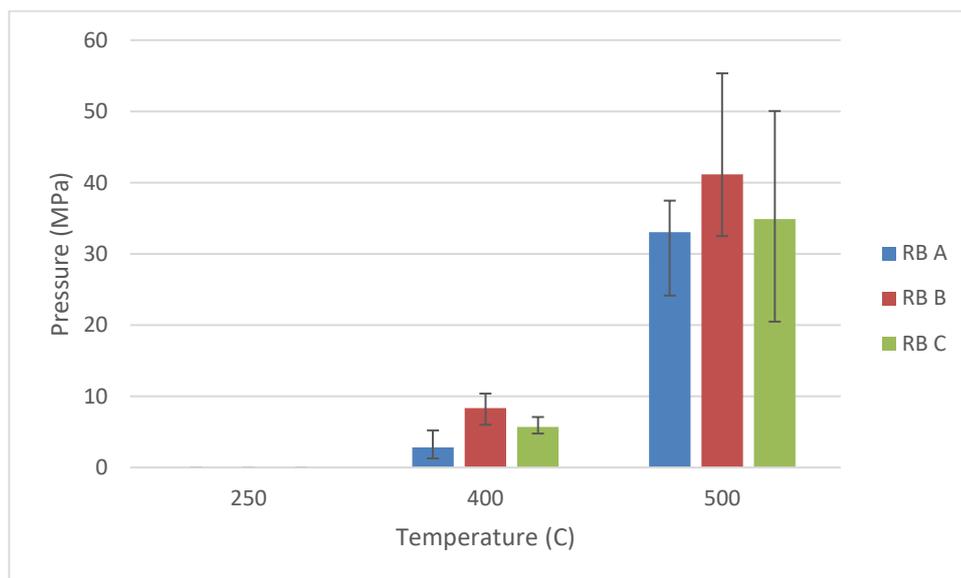


Figure 21: Amount of force (MPa) required to crush a pellet sintered at 250 °C for 24 h, 400 °C for 2 h and 500 °C for 2 h in a crush test.

In Figure 22, the effect of carbonate on the strength of the sintered pellets is presented. No correlation can be found between carbonate and sintered pellet strength. The strongest pellets were from RB B which did not have the highest carbonate. In Figure 23, the effect of chloride is shown. Chloride seems to have an increasing effect on the strength of sintered pellets. In Figure 24, the effect of potassium is explored. Potassium seems to have a decreasing effect on the strength of sintered pellets. These correlations need to be investigated further since there are only three dusts in this data.

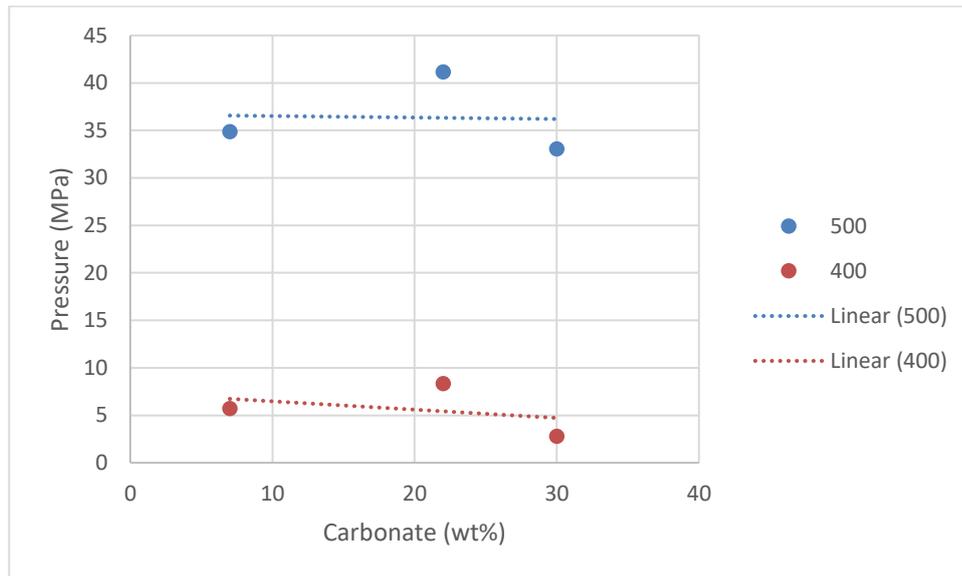


Figure 22: Negligible effect of carbonate on crush strength of pellets sintered at 500 °C and 400 °C.

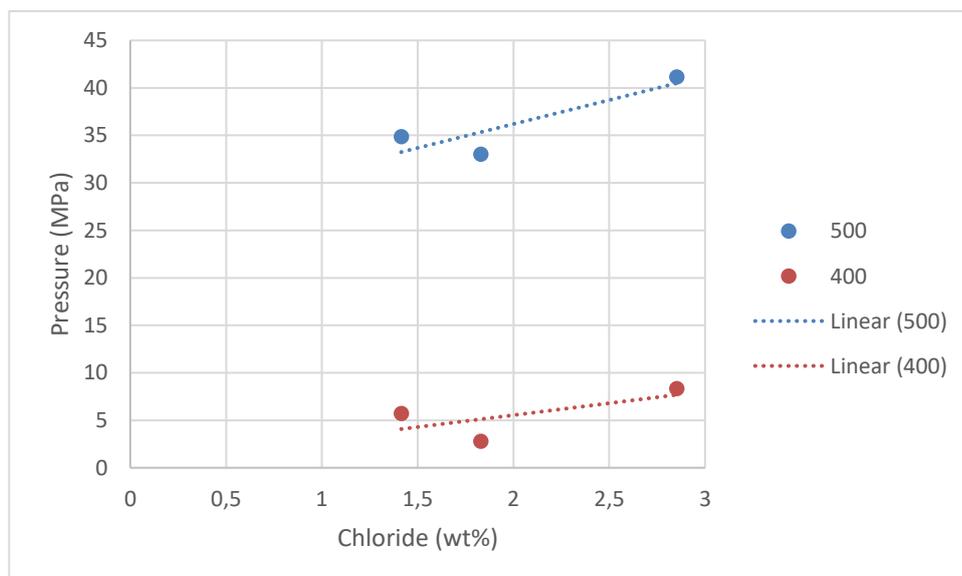


Figure 23: Small effect of chloride on crush strength of pellets sintered at 500 °C and 400 °C.

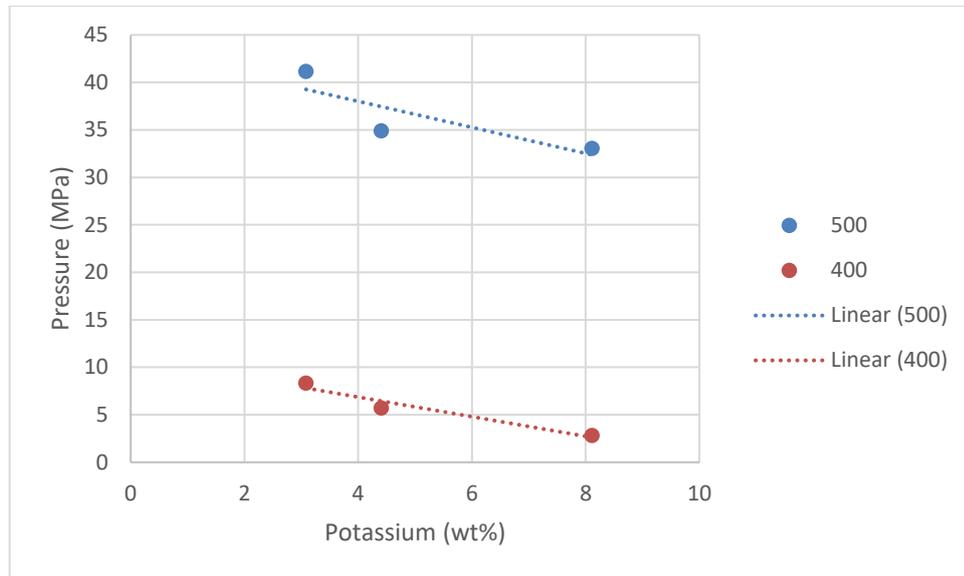


Figure 24: Small effect of potassium on crush strength of pellets sintered at 500 °C and 400 °C.

5 CONCLUSIONS AND RECOMMENDATIONS

The objective of this thesis was to shed some light on the observed new behavior of the dust and its relation to dust morphology and properties. The reason for the new fouling phenomena was not found. No clear differences that could indicate fouling were found in the composition and melting behavior of the dusts. Two of the boilers had very high levels of carbonate, however, the differences in dust carbonate were found not to significantly affect the sintering behavior of the dust. Chloride and potassium seem to have a small effect but needs to be investigated further. However, sintering due to temperature can be ruled out as the cause for the observed EP dust accumulation problems. Sintering does not occur in the EP solely due to temperature at 250 °C and below. The clearest difference is in the appearance of the dusts seen in the SEM images. Dust from the boiler which has fouling problems was more agglomerated than the other dusts. The pellets made from this dust were also observed to sinter to a slightly higher degree, measured as crush strength. This indicates that the degree of agglomeration in the dust is correlated to the crush strength after sintering.

For a more statistically significant study, dust from additional boilers should be analyzed. More work is also needed to explain the difference in the SEM images of the dusts. The differences in appearance can be connected to differences in dust formation. Determining where in the recovery boiler dust undergoes agglomeration could help the understanding of the problem. In-flight agglomeration of dust could hold answers.

SVENSK SAMMANFATTNING

Askans nedsmutsning av rökgaskanaler i sodapannor

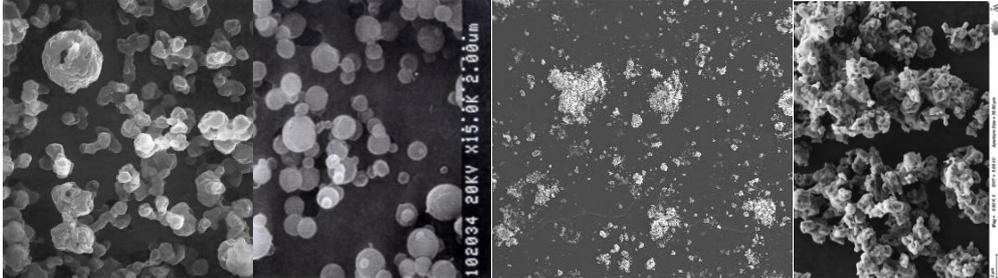
Inledning

I pannan i ett kraftverk kokas vatten som förångas och som kan användas för att generera elektricitet. Sodapannan är en del av en massafabrik som genererar elektricitet men också återvinner kemikalier. Sedan den första sodapannan uppfanns har storleken på pannan och mängden torrsbstans i bränslet, svartlut, ökat. Förändringen i torrsbstansen kan ses i tabell 1. Förbränning av svartlut ger upphov till aska. På senare tid har det börjat uppstå nedsmutsning i elektrostatiske utfällare (EP) och vattenvärmare (ECO). Detta beror på förändring i askans kemi och beteende. Förändring av askans utseende kan ses i bilderna från svepelektronmikroskop (SEM) i tabell 1. Aska har bland annat blivit lättare att fånga upp men svårare att avlägsna från filtren. Askan filtreras i EP som ser till att utsläppen hålls på en lämplig nivå. I en värld hotad av klimatförändringen är det viktigt att hålla koll på utsläppen.

Teknologier för att avdunsta så mycket vatten som möjligt ur svartlutet har utvecklats. Vattnet i ett bränsle förångas vid förbränning, vilket kräver energi, som annars kunde användas för att generera elektricitet. Därför är det viktigt att torka svartlutet. Vid förbränning av svartlut oxideras den organiska delen medan den oorganiska delen tappas ut som smälta i botten av ugnen. På grund av temperaturen i ugnen förångas en del oorganiska föreningar. Då temperaturen i ugnen höjs frigörs mera natrium och då den sänks frigörs mera svavel. Natriumet kan då reagera med koldioxid och bilda karbonat. När avgaserna och askan flödar vidare i pannan blir temperaturen lägre eftersom mera energi tas ut ur dem. När temperaturen är tillräckligt låg kan askan kondensera. Askan består till stor del av natrium, kalium, karbonat, sulfat och klorid. Förhårdning av aska kan bero på sintring. Sintrad aska kan leda till att den förhårdnas så att den inte längre går att avlägsna utan att stänga pannan och utföra dyra reparationer. Sintring av aska kan bero på temperatur, vilket undersöks i detta arbete.

Tabell 1: Förändringar i processen och askan i sodapannor från 1980-2012 *(Samuelsson, 2018), **2020 data från detta arbete.

(wt%)	~1980*	~1995*	2012*	2020**
Na	29	28.2	31	32.6
K	3.1	5.2	2	5.2
S	64.7	59.6	44.9	40.6
Cl	3.1	2.9	1	2
CO ₃	0.1	1.1	12.9	19.5
ds	63	73	76	80
SO ₂	high	low	0	0
Dust (g/Nm ³) dry	5-12	15-25	37.5	25-30



Syfte

Målet med detta arbete är att se om askan sintras genom sintringsexperiment med aska från olika pannor. Beroende på sammansättningen av askan från sodapannor kan sintring ske under smältpunkten. Meningen med detta arbete är att uppnå en fördjupad förståelse av askbildning i sodapannor samt askans kemiska och fysiska egenskaper.

Material och metoder

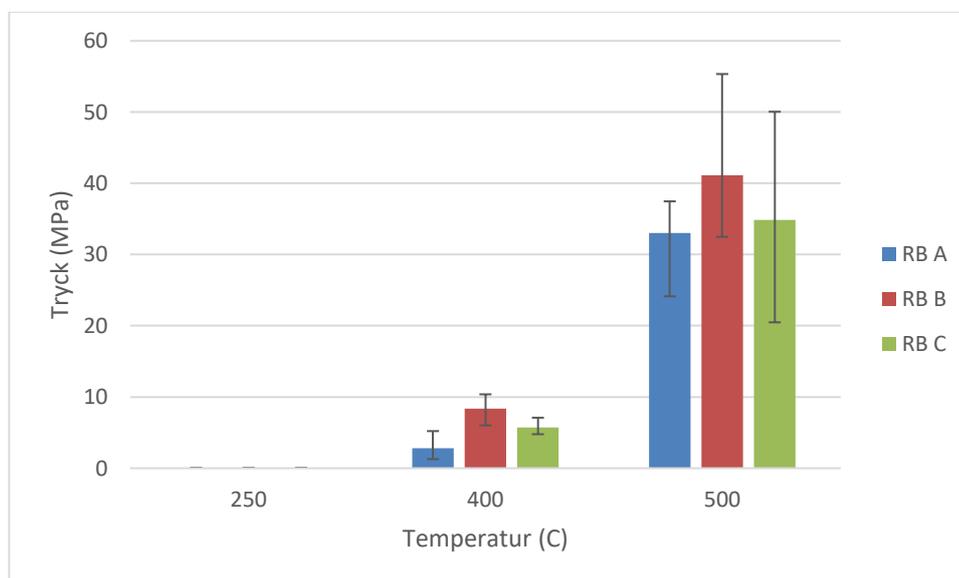
I experimenten torkades först aska från tre olika pannor. Därefter pressades askorna till piller som lades i ugn vid en viss temperatur och för en viss tid. Då tiden uppnåtts togs pillren ut, granskades visuellt och krossades. Om askan hade sintrats var det svårare att krossa pillren. För att räkna ut askornas smälttemperatur användes FactSage som kräver att askans sammansättning är känd. Sammansättningen mättes genom energispridande röntgenspektroskopi (EDXA). Vissa grundämnen kunde inte mätas med EDXA och räknades med hjälp av stökiometri. Bilder av askor togs med hjälp av svepelektronmikroskop (SEM). Värmemikroskop (HSM) användes för att ta reda på askornas sintringsbeteende.

Experiment

En testmatris gjordes för att hålla reda på vilka test som bör utföras. Den första planen var experiment i 150, 200 och 250 °C, det temperaturintervall som EP fungerar i. Det första experimentet gjordes i 250 °C i 24 timmar. I det förblev pillren oförändrade. I det andra experimentet användes vattenånga men ingen förändring i pillren kunde upptäckas. Eftersom ingen förändring kunde upptäckas vid 250 °C utfördes inga experiment i lägre temperaturer. Däremot utfördes experiment i 400 och 500 °C.

Resultat

Resultatet av experimenten visar att ingen sintring sker vid 250 °C och lägre för askorna. Resultatet bekräftas i HSM-analysen. Sintring sker i olika grad vid 400 och 500 °C. Mängden tryck som krävs för att krossa ett piller är relaterat till graden av sintring. Piller från sodapanna B, som enligt SEM-bilder har högst grad av sintring, kräver mera tryck för att krossas. Temperaturen på ugnen som pillren varit i har en större påverkan.



Figur 1: Mängden tryck (MPa) som krävs för att krossa piller som varit i ugn i en viss temperatur (°C)

Avslutning

Orsaken till askans nya beteende hittades inte. Att sintring inte sker vid 250 °C och lägre temperaturer tyder på att det är något annat fenomen som orsakar sintring. Inga tydliga skillnader som kan förklara nedsmutsningen hittades i askornas innehåll och smältbeteende. Mängden karbonat i två av askorna var väldigt hög, men eftersom en av pannorna har nedsmutsningsproblem men inte den andra, kan inga slutsatser dras. Den största skillnaden mellan askorna hittades i bilderna från svepelektronmikroskopet (SEM). Aska med det nya beteendet hade agglomererat mera än de andra askorna. Piller gjorda på denna aska krävde även högst tryck för att krossas. För att förklara skillnaderna i SEM bilderna bör mera arbete göras. Att ta reda på var i sodapannan askan undergår agglomeration kan ge svar på askans utseende.

REFERENCES

- Adams, T. N. et al., 1997. *Kraft Recovery Boilers*. 1st ed. Atlanta: Tappi Press.
- Alén, R., Rytönen, S. & McKeough, P., 1995. Thermogravimetric behavior of black liquors and their organic constituents. *Journal of analytical and applied pyrolysis*, Volume 31, pp. 1-13.
- Backman, R., Enestam, S. & Zevenhoven, R., 1998. *Structure and behaviour of inorganics in recovery boilers - a modeling approach*, Åbo: LIEKKI 2 Technical Review.
- Baxter, L., Hatch, G., Sinquefield, S. A. & Frederick, W. J., 2004. *An Experimental Study of the Mechanisms of Fine Particle Deposition in Kraft Recovery Boilers*. Charleston, International Chemical Recovery Conference.
- Duhamel, M., Tran, H. & Frederick, J. W. J., 2004. The sintering tendency of recovery boiler precipitator dust. *Tappi Journal*, 3(10), pp. 25-30.
- Ek, M., Gellerstedt, G. & Henriksson, G., 2009. *Pulp and Paper Chemistry and Technology vol. 2 Pulping Chemistry and Technology*. 1st ed. Berlin: De Gruyter, Inc..
- Frederick, J. W. J. & Vakkilainen, E. K., 2003. Sintering and Structure Development in Alkali Metal Salt Deposits Formed in Kraft Recovery Boilers. *Energy & Fuels*, 17(6), pp. 1501-1509.
- Frederick, W. J. J., Ling, A., Tran, H. N. & Lien, S. J., 2004. Mechanism of sintering of alkali metal salt aerosol deposits in recovery boilers. *Fuel*, Volume 83, pp. 1659-1664.
- Frederick, W. J. J., Vakkilainen, E. K., Tran, H. N. & Lien, S. J., 2004. The Conditions for Boiler Bank Plugging by Submicrometer Sodium Salt (Fume) Particles in Kraft Recovery Boilers. *Energy & Fuels*, 18(3), pp. 795-803.
- Grace, T. M., Cameron, J. H. & T., C. D., 1985. *Char Burning*, s.l.: The Institute of Paper Chemistry, Project 3473-6, Summary Technical Report.
- Hupa, M., 2004. *Research highlights in recovery boiler chemistry*. Helsinki, Kyriiri Oy.
- Hupa, M., 2007. Recovery boiler chemical principles. *TAPPI Kraft Recovery Course*

2007, Volume II.

Hupa, M., Solin, P. & Hyöty, P., 1987. Combustion behavior of black liquor droplets. *Journal of Pulp and Paper Science*, 13(2), pp. 67-72.

Khalaj, A., Kuhn, D. & Tran, H., 2006. Composition of carryover particles in recovery boilers. *Journal of pulp and paper science*, 32(2), pp. 90-94.

Kochesfahani, S., Tran, H. & Jones, A., 2000. Particulate Formation During Black Liquor Char Bed Burning. *Journal of pulp and paper science*, 26(5), pp. 180-187.

Leppänen, A., 2015. *Modeling Fume Particle Dynamics and Deposition with Alkali Metal Chemistry in Kraft*, Tampere: Tampere University of Technology.

Mikkanen, P., 2000. *Fly ash particle formation in kraft recovery boilers*, ESPOO: VTT PUBLICATIONS.

Mikkanen, P., Kauppinen, E. I., Pyykönen, J. & Jokiniemi, J. K., 1999. Alkali Salt Ash Formation in Four Finnish Industrial Recovery Boilers. *Energy & Fuels*, 13(4), pp. 778-795.

Salmenoja, K., 2016. *Cross Technology Training Recovery Boiler*, Vierumäki: ANDRITZ Pulp & Paper.

Samuelsson, I.-L., 1999. Effect of Salt Cake Properties on Precipitator Performance. *Pulp and Paper Technical Association of Canada*, 86(C).

Samuelsson, I., 2018. *Processförändringar för sodapannan - Nya utmaningar för elfiltren*, s.l.: s.n.

Samuelsson, I. L., Johansson, F., Levesque, D. & van Hattem, V., 2014. *Effect of Black Liquor Firing Conditions on Salt Cake Properties*. s.l., International Chemical Recovery Conference.

Saw, et al., 2010. Influence of droplet size on the release of atomic sodium from a burning black liquor droplet in a flat flame. *Fuel*, Volume 89, pp. 1840-1848.

Tamminen, T., 2002. *Continuous Monitoring of Dust Concentration and Composition in Kraft Recovery Boilers*, Åbo: Åbo Akademi Process Chemistry Group.

Tamminen, T. et al., 2002. Dust and flue gas chemistry during rapid changes in the operation of black liquor recovery boilers. Part 1. Dust formation. *Tappi Journal*, 1(5),

pp. 27-31.

Tavares, H. et al., 1996. Fume chemistry, morphology and deposition in a kraft recovery boiler.. *Pulp Paper Can*, 97(10), pp. 361-366.

Techakijajorn, U., Frederick, W. & Tran, H., 1999. Sintering and Densification of Recovery Boiler Deposits: Laboratory Data and a Rate Model. *Journal of Pulp and Paper Science*, 25(3), pp. 73-80.

Tran, H., 2007. Recovery boiler fireside deposits and plugging prevention. *Tappi Kraft Recovery Course*, Issue 2007, pp. 537-572.

Tran, H. et al., 2000. *Relationship between SO₂ emissions and precipitator dust compositions in recovery boilers*. Atlanta, GA, TAPPI Engineering Conference.

Tran, H., Gonsko, M. & Mao, X., 1999. Effect of composition on the first melting temperature of fireside deposits in recovery boilers. *TAPPI JOURNAL*, 82(9), pp. 93-100.

Vakkilainen, E., 2010. Predicting Ash Properties in Recovery Boilers. *International Chemical Recovery Conference*, Volume 2, pp. 237-245.

Vakkilainen, E. K., 2005. *Kraft recovery boilers - Principles and practice*. 1st ed. Helsinki: Suomen Soodakattilayhdistys r.y..

Wessel, R. et al., 2004. *Particle Formation And Deposition In Recovery Boilers*. Charleston, South Carolina, International Chemical Recovery Conference.

Zevenhoven, M., Yrjäs, P. & Hupa, M., 2010. Ash-Forming matter and Ash-Related Problems. In: M. Lackner, F. Winter & A. K. Agarwal, eds. *Handbook of Combustion*. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA, pp. 493-531.

APPENDICES