

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Dusting in a lime kiln

Characterization of the material and unit operations

HENRIC DERNEGÅRD

Forest Products and Chemical Engineering
Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2019

Dusting in a lime kiln
HENRIC DERNEGÅRD

© HENRIC DERNEGÅRD, 2019.

Licentiatuppsatser vid Institutionen för kemi och kemiteknik
Chalmers tekniska högskola.
Nr 2019:07

Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Cover: Lime kiln no.2 at the Mönsterås mill, seen from the burner end.

Chalmers Reproservice
Gothenburg, Sweden 2019

Dusting in a lime kiln

Characterization of the material and the unit operations

HENRIC DERNEGÅRD

Forest Products and Chemical Engineering

Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Abstract

The present thesis describes the background of, and gives some points of orientation for, the phenomenon of dusting in the burner zone of a lime kiln. The aim of this study is twofold: to increase knowledge of the factors that influence the degree of dusting and also to investigate the effect a dusting lime kiln has on the white liquor preparation process.

The thesis covers parts of the historical development in the recovery process, earlier findings on dusting in the literature, the impact of dusting on the causticizing process and an explanation for the cause of dusting along with actions to avoid, or contain, it.

A Kraft pulp mill utilizes a rotary lime kiln to regenerate CaO from CaCO₃ by reburning. The CaO is used to regenerate the cooking chemicals for the digester. A lime kiln is around 70-100 meters long and around 2-4 meters in diameter. The kiln is typically equipped with product coolers at the discharge end where hot reburned lime meets incoming secondary air in a counter-current heat-exchange process.

Dusting in a lime kiln occurs when fine material chaotically swirls at the discharge end of the kiln. This is caused when the velocity of upward moving air through the discharge exceeds the terminal velocity of the material that drops back into the kiln from the product coolers. The reason for material dropping back is that some material remains in the cooler opening and is not transported further into the cooler, as intended. Both the terminal velocity and the tendency to get stuck in the product cooler inlet are connected to the size of the reburned lime. If the lime is powdery fines, dust will be formed in the burner zone. If the lime forms nodules, which is intended, dusting will not occur.

A dusting kiln produces a fine particulate reburned lime that is very hard burned and has a low specific surface area. When this lime is slaked, the slaking and causticizing reaction is slower and might lead either to a lower yield of effective alkali or to a slower temperature rise in the slaker, and potential overliming. It is found that when dusting occurs in a kiln, the amount of material inside the kiln increases notably even though the feed rate of lime mud has not increased.

Furthermore, during dusting conditions, the reburned lime mud contains a very large fraction of fine material. A possible explanation for the increased load could be that the fine material is present in a large part of the kiln. The fine material is likely subjected to stronger friction than the nodules. This in turn will lead to a slower material transport through the kiln and thus an increased amount of material inside the kiln.

Through mill trials, it is found that removing the recirculated material from the electrostatic precipitator for a couple of hours has a positive effect on bringing a dusting kiln back to a clear one.

Keywords: Dusting lime kiln, ESP-dust, fines, terminal velocity, lime mud filter, reactivity

List of publications

This thesis is based on the work presented in the following publications, referred to by Roman numerals in the text.

- I. Characterization of a dusting lime kiln: A mill study
Henric Dernegård, Harald Brelid and Hans Theliander
Nordic Pulp & Paper Research Journal, 32(1): 25-34, 2017
- II. Variability in lime mud feed rate induced in the lime-mud filter: Consequences and actions
Henric Dernegård, Harald Brelid, Hans Theliander and Erik Berg
Journal of Science & Technology for Forest Products and Processes, 6(3): 19-27, 2017

Work related to this thesis has also been presented at the following conferences:

- i. Variability in lime mud feed rate induced in the lime-mud filter: Consequences and actions
Henric Dernegård, Harald Brelid, Hans Theliander and Erik Berg
International Chemical Recovery Conference, Halifax, NS, Canada, May 24-26, 2017
- ii. Characterization of a Dusting Lime Kiln: A Mill Study
Henric Dernegård, Harald Brelid and Hans Theliander
TAPPI PEERS, Norfolk, VA, USA, November 5-8, 2017

Table of Contents

1	Introduction	1
1.1	Background	1
1.2	Objectives and outline	4
2	Recovery of cooking chemicals in the kraft process	5
3	Materials and methods	7
3.1	Mill description	7
3.2	Liquor samples	7
3.3	Reburned lime and lime mud samples	8
4	Literature review.....	10
4.1	Slaking and causticizing.....	10
4.1.1	On the equilibrium	10
4.1.2	On the kinetics in slaking and causticizing	10
4.1.3	On the lime charge.....	11
4.2	Around and in the lime kiln.....	13
4.2.1	On the calcination temperature	13
4.2.2	On the sintering and granulation of lime	15
4.2.3	On the lime mud filter and process stability.....	17
4.2.4	Non-process elements	17
5	Results and discussion	20
5.1	Dusting in the hot end of the lime kiln	20
5.1.1	Physical prerequisites for dust formation.....	20
5.1.2	Extent of granulation in the lime kiln.....	22
5.1.3	Slaking and causticizing of reburned lime fractions from clear and dusting periods ...	23
5.1.4	Cause of dusting.....	26
5.2	Process stability in the kiln.....	33
5.2.1	Variations in lime mud filter and feed-end temperature	33
5.2.2	Effects of shutting off the dilution water to the vat of the lime mud filter.....	35
6	Main conclusions	37
7	Future work.....	38
8	Acknowledgements.....	39
9	References	40
10	Summary of Papers I and II	43
10.1	Paper I	43
10.2	Paper II	44

1 Introduction

1.1 Background

From a global perspective, the pulp and paper industry is one of the five most energy intensive industries (International Energy Agency, 2015) and has specifically been identified as offering a significant potential for reducing CO₂-emissions by replacing fossil fuels with internal biofuels (International Energy Agency, 2009). Domestically, the pulp and paper

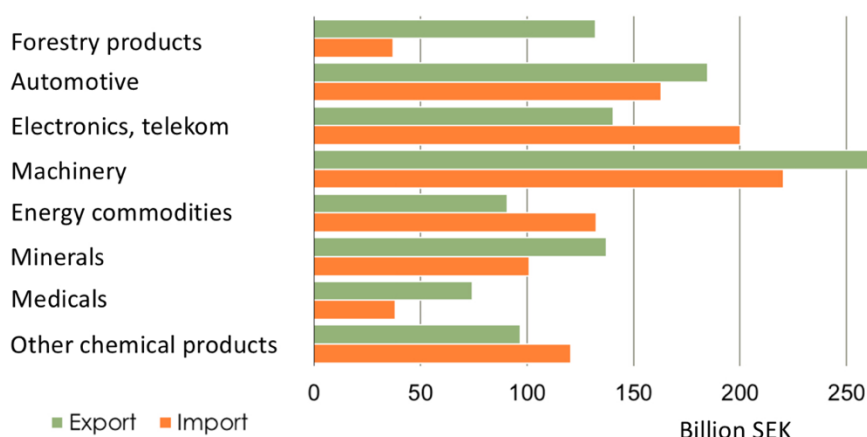


Figure 1: Import and export value for different industry sectors (Skogsindustrierna, 2018)

industry is of crucial importance for the Swedish economy. Forestry industries (of which pulp and paper is the largest sector) have a huge net export value compared to other important industries, see Figure 1. Furthermore, it has approximately 10% of the total industrial investments in Sweden.

The production of market pulp in Sweden has increased by 2.4% annually from 1980 to 2017 (Skogsindustrierna, 2018) and is projected to grow by 2.3% annually from 2017 until 2045 (Ankerfors et. al., 2018). This is approximately twice the growth rate compared to that of chemical pulp, which is projected to grow by around 1.3% annually (Thuresson and Johansson, 2016).

As seen in Figure 2, the Swedish pulp and paper industry produced 10.3 million metric tons of paper in 2017 whereof 9.4 million metric tons were exported. The production of pulp was around 12.1 million ADt whereof market pulp was 4.3 million ADt. The export accounted for 3.7 million ADt, thus approximately 600 000 ADt of market pulp was used in Swedish paper mills.

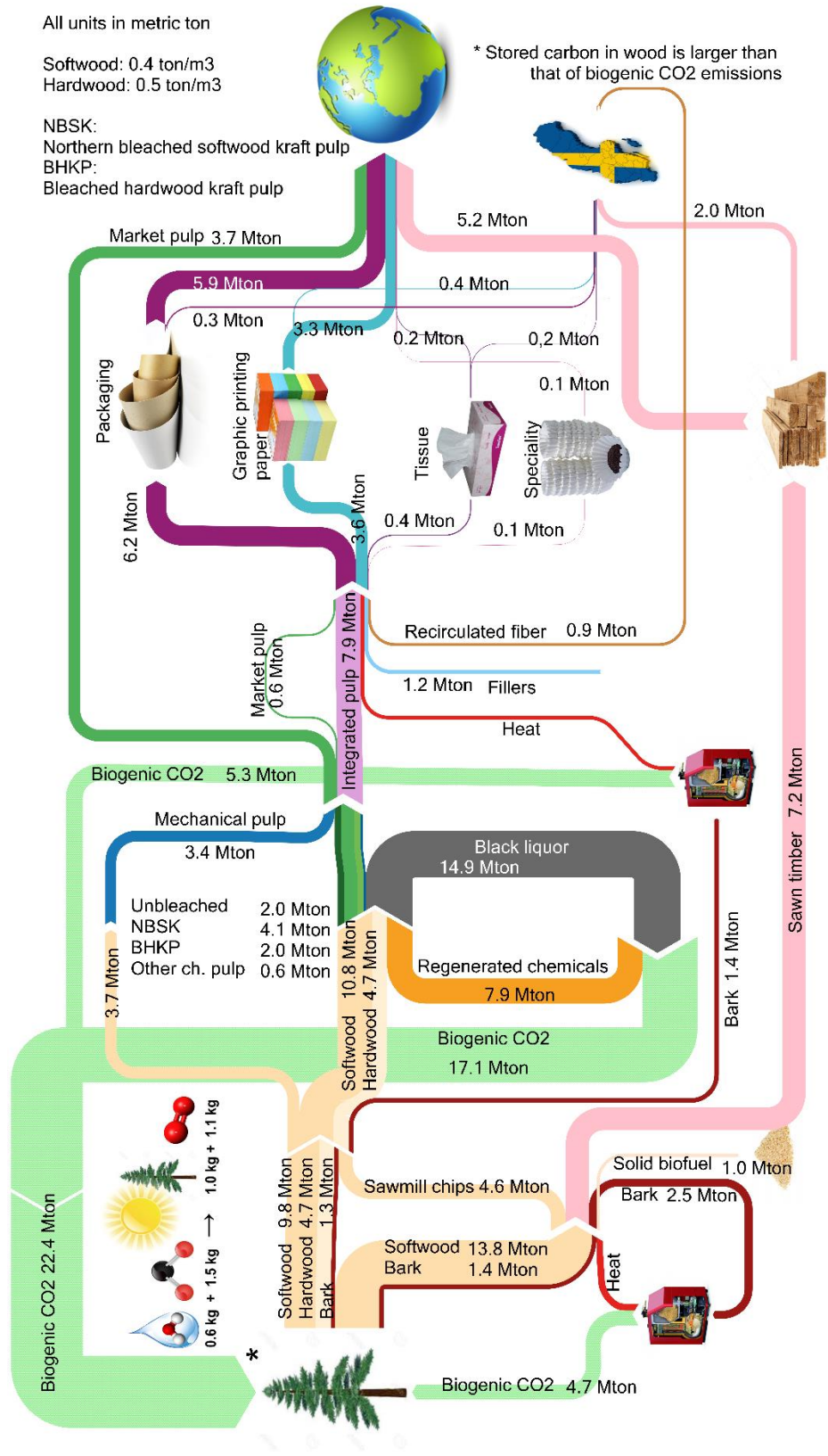


Figure 2: Material flow of Swedish forest industry. Production and sales of pulp and paper and sawn timber. Numbers expressed as dry solids and referring to 2017. The total felling was 90.9 million m³ stemwood with bark. The collected volume was 72.8 million m³ under bark whereof 36.7 was sawn timber and 28.2 was pulp wood. Data collected from Skogsindustrierna (2017) and Skogsstyrelsen (2019).

The pulp and paper industry is the most energy intensive Swedish industry using an annual 73.2 TWh (Energimyndigheten, 2017), which is more than 50% of the energy used in the industry sector (Table 1).

Table 1: Energy use and losses in the Swedish energy system for the year 2015. The difference between the final use and the added energy is mainly the energy used in power plants to produce power and heat, which in turn are used in the different sectors. Data collected from Energimyndigheten (2017) and Skogsstyrelsen (2017).

2017 (TWh)	Biofuels	Coal and Coke	Petroleum products	Fossil gas	Other fuels ¹	District heating	Electricity ²	Total
Industry	56	13	10	6	6	3	50	144
non-energy ³	-	-	36	3	-	-	-	39
Energy prod.	(53)	(18)	(228)	(8)	(195)	(4)	(65+18)	589
Internal use ⁴	-	-	(1)	(1)	-	-	(10)	10
Trans. loss. ⁵	-	-	-	(1)	-	(7)	(11)	19
Others ⁶	14	-	7	1	-	46	72	140
Transport	19	-	66	-	-	-	3	88
Tot. end use ⁷	89	13	87	8	6	50	126	379

¹ "Other fuels" also include 184 TWh nuclear fuel. Around ⅓ become energy losses in nuclear power plants.

² 65 TWh hydropower and 18 TWh windpower.

³ Fossil fuels for non-energy use purposes, such as production of methanol for chemicals.

⁴ Internal energy use in the energy sector.

⁵ Transformation- and distribution losses in energy distribution.

⁶ Others includes residential, agriculture and farming, construction, public sector and housing.

⁷ The total use of biofuels is 89 + 53 TWh. 7.5 million m³ under bark was from stemwood (2-2.4 MWh/m³, Thuresson and Johansson, 2016).

The production of Kraft pulp also involves the production of 14.9 million metric tons DS of black liquor (Figure 2). Using the lower heating value from Table 2, this represents around 50 TWh black liquor. Thus, the major part of the energy demand in a pulp mill is covered by the latent heat of black liquor.

Table 2: Elemental composition of black liquor solids, heating values of black liquor solids and ratio between black liquor solids and pulp, for softwood (SW) and hardwood (HW). Data collected from Mönsterås mill production system.

	C	H	N	S	CL	NA	K	O	HHV	LHV	Black liq.
	w%	w%	w%	w%	w%	w%	w%	w%	GJ/t	GJ/t	tDS/ADt
SW	33	4	0.05	5	0.15	19.5	1.8	36.5	13.5	12.5	1.85 - 1.9
HW	31	4	0.1	5	0.15	19.75	12	38	12.5	11.5	1.5 - 1.6

However, one unit operation in the Kraft pulp mill is still dependent on external fuel, the lime kiln. Mainly liquid fuels are used in this unit, making it a point of interest for substitution with low value internal fuels. With a specific reburned lime demand of 0.28 t/ADt of Kraft pulp (Dernegård et al., 2017), around 2.2 – 2.3 million metric tons of lime is produced in Sweden. Assuming an average specific heat demand of 6.5 GJ/ton of reburned lime, this implies that around 4 TWh of fuel is used in the lime kiln. 1 TWh thereof is solid fuel, 2 TWh is liquid fossil fuel and 1 TWh is bio-oil.

Sweden has an ambitious energy target of being net fossil free in 2045. To reach this target, around 20 TWh of upgraded bio fuels (Wiesner and Edfeldt, 2019) must be made accessible to the industry sector. The transition from liquid fuels to internal solid fuel in Swedish lime kilns would make between 3 and 4 TWh available for alternative use. For comparison, the combined production of liquid or gaseous biofuels, such as biodiesel, bioethanol or biogas, from the entire Swedish forestry industry was approximately 1 TWh in 2017 (Energimyndigheten, 2017).

By using solid biomass, such as bark or sawdust, as the fuel in a lime kiln, significant amounts of liquid fuel, fossil fuels or biofuels, can be made available for alternative use. Bark is by far the lowest value material in the mill that can be used for combustion. However, to the author's knowledge, the Södra Cell mill in Mönsterås is the only mill using pulverized bark as the fuel in a lime kiln today.

The main obstacles to transitioning from external liquid fuels to internal solid fuels are potential process variability (Manning & Tran, 2014) and intake non-process elements that come with the solid fuel and affect the chemical composition and reactivity of the reburned lime, which, in turn, influences the production and quality of white liquor (Francey et al., 2009).

Along with higher production rates in the pulp mill and lime kilns, dusting at the hot end of the kilns has been observed at Södra Cell Mönsterås. It is, however, not known if this is due to the use of bark as fuel. Furthermore, it is not known to which extent the dusting has an effect on white liquor quality. No information regarding the impact of dusting at the hot end of the kiln could be found in the literature, and, therefore, the present thesis project was initiated.

1.2 Objectives and outline

The objective of this study is to

- investigate the effect of dusting at the hot end of a kiln on the quality of white liquor
- investigate the cause of dusting in a lime kiln
- suggest measures to contain the effects of dusting
- investigate factors that influence the process stability of the lime mud filter

This thesis is mainly based on the two appended papers however, some additional data is included: primarily data extracted from the production and lab data system at the Mönsterås mill.

A brief description of the recovery of cooking chemicals in the Kraft process is given in Chapter 2, and material and methods along with a description of the mill are given in Chapter 3. Chapter 4 is a review of the relevant literature, and Chapter 5 presents a discussion of the findings of this work. Chapter 6 summarizes the main conclusions, and Chapter 7 presents some suggestions for future work that should be performed to further increase knowledge on this topic.

2 Recovery of cooking chemicals in the kraft process

This chapter gives an overview of the Kraft pulping process and the recovery of cooking chemicals in particular. Figure 3 shows the pulp digester and the major unit operations in the chemical recovery cycle of the Kraft process.

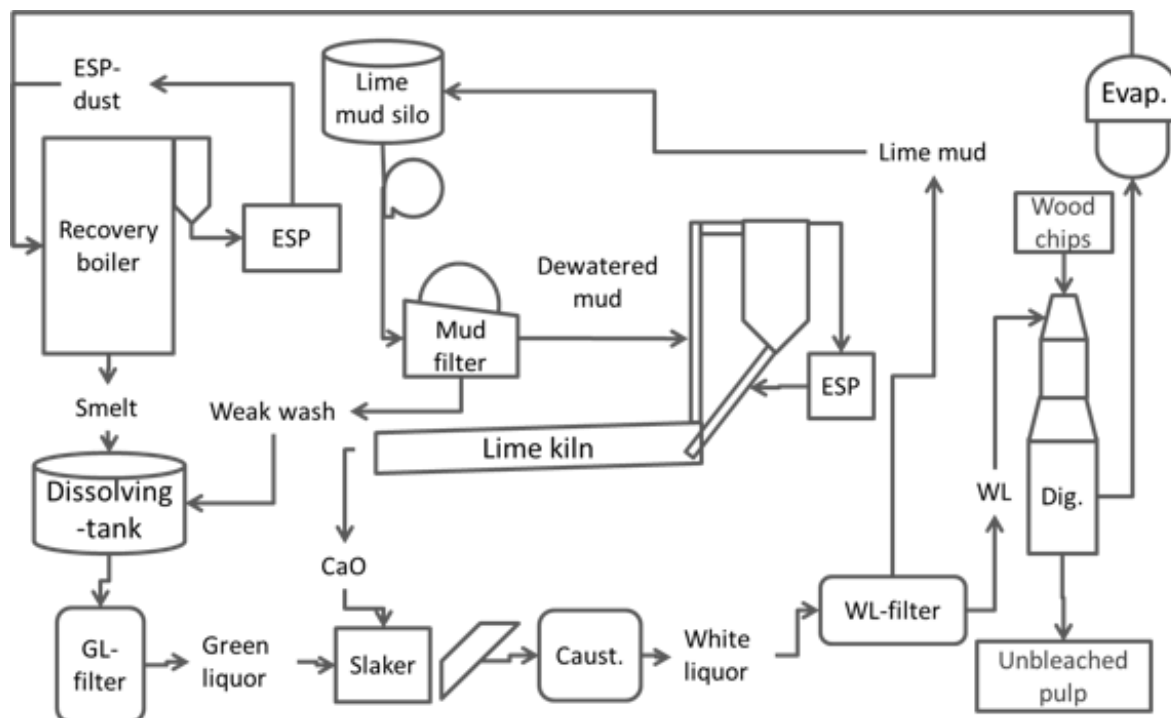


Figure 3: Schematic depiction of chemical recovery cycle

In the Kraft process, wood chips are mixed with white liquor containing the active ions OH^- and HS^- . During digestion, the active ions react with lignin, as well as, to some extent, carbohydrates, which to various extents are fragmented and dissolved. The reactions during digestion lead to the fragmentation and dissolution of lignin, which facilitates the liberation of cellulose fibers suitable for paper production. The spent cooking liquor is called black liquor. A typical black liquor from softwood contains around 33% inorganics, a large part of which is sodium salts, 30% lignin and 30% various carboxylic acids (reaction products from carbohydrate degradation) and around 7% other organics, such as extractives and some xylan (Niemelä & Alén, 1999). Black liquor is evaporated to a high dry solids content and incinerated in a recovery boiler for the regeneration of cooking chemicals and production of steam. The recovery boiler produces an inorganic salt smelt that is dissolved in water to form “green liquor,” which contains HS^- , OH^- and CO_3^{2-} . In order to convert the carbonate ions to hydroxide ions, reburned/burned lime (CaO) is added to the white liquor, the calcium oxide is slaked and forms calcium hydroxide, which in turn reacts with the carbonate ions, forming hydroxide ions and calcium carbonate (lime mud).

In the very early days of Kraft pulping, causticizing was a batch-wise process where lime was burned in an external kiln and transported manually in baskets. The lime was unevenly burned with high degrees of uncombusted fuel, mainly coke. The work was physically hard and the impact on the environment was high. In order to move away from manual handling of the burned lime, continuous slaking and causticizing of the lime entered the market. The

Tomilson recovery boiler was introduced in the 1940s, thereafter came the common practice of reburning of lime mud in rotary kilns. The first rotary kiln in the world was built in Skutskärsverken in Sweden, already in 1905. Rotary kilns in kraft pulp mills were, however, not commonly in use until the 1940s (Borg & Hult, 1985). Separation between white liquor and the formed lime mud was, in the beginning, done with thickeners, but later (starting during the 1960s) thickeners were replaced with filters.

When mills installed filters, a common experience was that filterability was improved when burning the lime harder, which could be achieved by increasing the hot end temperature. However, a consequence of this was more frequent formation of rings in the burner zone. Environmental focus in the 1980s pushed for burning of stripper gas and digester off-gas in the lime kiln instead of simply emitting these gasses, which contained e.g. hydrogen sulfide and organic sulfides, to the atmosphere. The burning of these gasses in the lime kiln often resulted in variations in heating value and necessitated increased focus on process control. Quite early, it was found that the dewatering and washing of the lime mud on lime mud filters was one important factor in stabilizing fuel demand and minimizing emissions of H₂S. With improved washing, impaired nodulization and dusting of fine particulate lime with subsequent difficulties in regulating the temperature in the kiln were reported (Carlhamn, 1980).

3 Materials and methods

This is a single mill study, and the Mönsterås mill is the subject of the sampling and investigation. The mill was chosen because it is the only mill, to the knowledge of the author, where the main fuel in the lime kiln is pulverized bark.

The mill is introduced in this chapter, and a description of the investigated materials and the analytical procedures applied are given.

3.1 Mill description

Södra Cell mill in Mönsterås produces 750 000 air dry metric tons (ADt) of fully bleached pulp per year, of which 200 000 ADt are hardwood pulp and 550 000 ADt are softwood pulp. There are two lime kilns that both use a mix of pulverized hardwood bark (70%) and tall oil pitch (30%) as fuel. As seen in Table 3, the hardwood bark has a higher heating value than the bark and sawdust from softwood, but a considerably lower value than the heating value of the tall oil pitch.

Table 3: Analysis of fuels used at Mönsterås mill. The analyses were performed at RISE.

	HHV	LHV	C	H	N	O	S	Ash
	GJ/t	GJ/t	w%	w%	w%	w%	w%	w%
Tall oil pitch	40.0	38.5	80	11	0.05	9	0.2	0.2
Softwood sawdust	20.5	19.1	50	6	0.05	43	<0.01	0.3
Pulverized hardwood bark	22.3	21.0	55	6.5	0.5	35	0.03	3
Pulverized softwood bark	20.6	19.3	52	6	0.4	38	0.03	3.5

Kiln no.1 is 113 meters long, has an inner diameter of 3.3 meters and a production rate of 450 metric tons of burned lime per day. Kiln no.2 is 73.5 meters long, has an inner diameter of 2.8 meter and a production rate of 250 metric tons per day. Kiln no.1 is equipped with a labyrinth cooler and Kiln no.2 has satellite coolers. Both kilns are equipped with a flash dryer, an electrostatic precipitator (ESP) and a lifter section in the lime mud feed end of the kiln. The calculated adiabatic flame temperature is about 1800°C for dry bark fuel and somewhat higher with the addition of 30% tall oil pitch due to the higher heating value. The flue gas temperature is about 700°C in the lime mud feed end. The lime production is equal to 280 kg of burned lime per ADt for softwood and slightly lower for hardwood pulp.

3.2 Liquor samples

At the Mönsterås mill, the green and white liquor is sampled every 10 minutes and the composition is determined with a FT-NIR measuring device. The values presented in Table 4 are the results of a sampling series that were analysed using ABC titration according to SCAN-N 30:85 and an FTPA2000-260 instrument from FITNIR. Table 3 also shows the calculated ionic strength and the equilibrium constant, K_c , at two different temperatures. K_c is calculated according to Eq. 4 in section 4.1.1. In Paper 1, K_c was calculated in this way for designing experiments far away and in the vicinity of the equilibrium point in causticizing.

Table 4: Composition of green liquor, NaOH, Na₂CO₃ and Na₂S are measured with ABC titration. Na₂SO₄ and Na₂S₂O₃ are measured with FT-NIR.

Component	g/liter as NaOH	g/liter as substance	g/kg as substance
NaOH	5.3	5.3	4.6
Na ₂ CO ₃	106	140.4	122.1
Na ₂ S	52.4	51.1	44.4
Na ₂ SO ₄	3.8	6.8	5.9
Na ₂ S ₂ O ₃	1.8	3.6	3.1
Ionic strength			4.89 (mol/kg)
Equilibrium constant (K_c) at 20 °C			36.1 (mol)
Equilibrium constant at (K_c) 103 °C			26.7 (mol)

A slaking and causticizing study was conducted to investigate the effect of a dusting lime kiln on the production of white liquor. The lime was slaked to Ca(OH)₂ and causticized in an Dewar flask under continuous agitation.

3.3 Reburned lime and lime mud samples

Samples of reburned lime were taken from the sample point of the accept size (smaller than around 5 cm) after the product coolers, and the dewatered lime mud was sampled directly from the lime mud filter, ensuring that the entire filter width was covered, and the ESP dust was sampled from the ESP-reflux elevator (Figure 4).

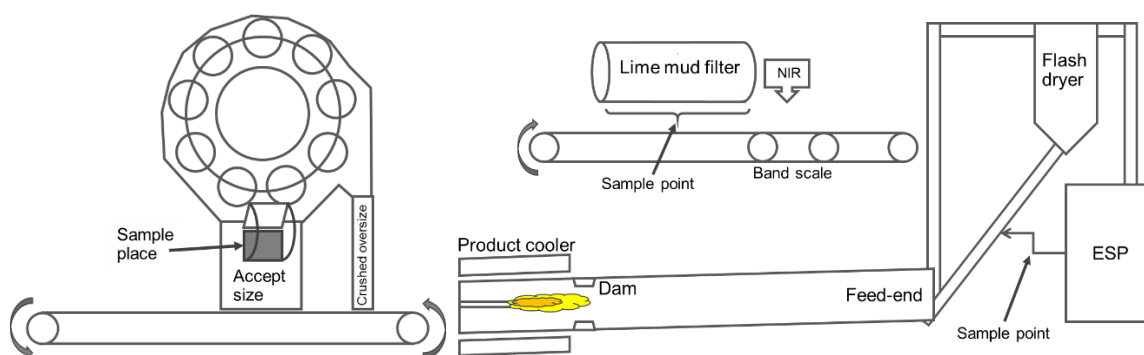


Figure 4: Depiction of sample points

The reburned lime was collected in 5-liter steel bins, and the agglomerate size was determined with a standard sieve. The fractions were as follows: larger than 15 mm, between 10 and 15 mm, between 1 and 10 mm and smaller than 1 mm. The analysis of the chemical elements in the reburned lime was performed with a PerkinElmer inductively coupled plasma (ICP) Optical Emission Spectrometer Optima 7300 DV in which 0.5 grams of lime was dissolved in 25 ml of a solution containing equal parts of hydrochloric acid (37%-concentration) and water. The sulfur and carbon contents were determined using an ELTRA CS 800 instrument where a completely dry sample was heated in an induction oven at 800°C under the addition of oxygen. The formed SO₂ and CO₂ was measured. The water-soluble sodium was analyzed using a Sherwood flame photometer 410.

The particle size distribution of the lime mud and ESP dust was measured using a Malvern Mastersizer 2000. The density of the solid material of the reburned lime was measured using an AccuPyc II 1340 pycnometer from Micrometrics.

Samples of the lime mud, ESP dust and reburned lime of particular interest were investigated with a FEI Quanta200 ESEM (environmental scanning electron microscope) and the specific surface area was measured using the Brunauer, Emmet and Teller method with nitrogen as the adsorption gas in a Micrometrics Tristar 3000.

4 Literature review

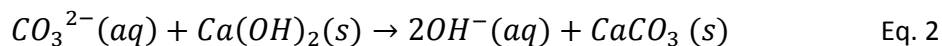
This chapter is divided between the literature on slaking and causticizing of green liquor and the literature on the processes involved in producing reburned lime.

4.1 Slaking and causticizing

4.1.1 On the equilibrium

Slaking and causticizing is the unit operation in chemical recovery where green liquor is converted to white liquor. The causticizing degree is a practical key indicator to monitor the performance of the causticizing plan, it answers the question of how much of the carbonate ions are converted to hydroxide ions. Since white liquor is the purpose of chemical recovery and the stability and quality of the white liquor production is a prerequisite for the performance of the Kraft process, it is a natural starting point of this literature review.

The slaking reaction is given by Eq. 1 and the causticizing reaction is given by Eq. 2. The causticizing reaction is believed to be one of the earliest equations described in technical literature relating to alkaline pulping processes and was mentioned as early as 1888 (Hammond, 1888).



The reaction reaches an equilibrium where the equilibrium constant is given in Eq. 3.

$$K_c = \frac{[OH^-]^2}{[CO_3^{2-}]} \quad \text{Eq. 3}$$

Theliander (1988a) found that diffusion is the rate determining step. The influence of temperature and ionic strength on the equilibrium constant can be calculated by Eq. 4 (Theliander, 1992).

$$\ln K_c = (2.67 + 915T) - (0.074 + 82.4T) \times I_c^{1.15} \quad \text{Eq. 4}$$

Theliander (1992) and Lindberg and Ulmgren (1986) studied the equilibrium of the causticizing reaction and found that a higher concentration of Na^+ and K^+ in the green liquor yields a lower equilibrium constant, resulting in a lower yield of OH^- ions.

4.1.2 On the kinetics in slaking and causticizing

Theliander (1988a) found that the slaking and causticizing reactions are both heterogeneous reactions where the diffusion of ions in the solid phase is the determining step in the overall causticizing rate.

In a study by Andersson et al. (1983), the temperature increase after slaking 6 different sets of reburned lime was measured, and the time to reach a steady state in the slaker (slaking time) was noted. The lime mud had been burned at different temperatures in N_2 or in air and SO_2 for 2, 3 or 5h. The temperature, at which the slaking time increased dramatically was denoted the *critical temperature*. The findings by Andersson et al. show that the critical temperature is around 1300°C for lime reburned for 3h in N_2 .

When slaking lime that was reburned in the presence of SO_2 , the critical reburning temperature was lower. This indicates that SO_2 enhances sintering. For lime reburned above this critical temperature, the time in the slaker to reach a stable temperature increased in proportion to the residence time in the reburning oven, indicating that the lime was hard burned or, perhaps, partially dead burned. Below the critical temperature, however, the slaking time was only marginally affected by the reburning time

These results are very similar to those of Lindberg and Ulmgren (1986) who found that while the slaking time of calcined pure CaCO_3 was practically unaffected by the reburning temperature (atmosphere and residence time was, however, not noticed in that paper), the slaking time for industrial lime mud changes drastically as the reburning temperature exceeds 1300°C . In addition to the reactivity of the lime, Lindberg and Ulmgren have also found that the temperature in the slaker is the strongest contributing factor and increases the reaction rate 2-3 times with a temperature increase from 97°C to 120°C . They also investigated the effect of cation concentration ($\text{Na}^+ + \text{K}^+$) and found that it has no significant effect on the reaction rate. The cation concentration, however, has a great impact on the equilibrium of the causticizing reaction since the increase in ionic strength decreases the equilibrium constant as shown in Eq. 4

4.1.3 On the lime charge

Adequate lime charge is a topic of interest since it directly affects the need for fuel to the lime kiln and, indirectly, since process variability can be induced in the causticizing plant. Rydin et al. (1977) slaked and causticized different limes in a synthetic green liquor and investigated, among other things, the effect of the lime charge. They concluded that, when the molar ratio of CaO to Na_2CO_3 exceeds one, the conversion degree of Na_2CO_3 to NaOH remains almost constant at a level slightly higher than 80%.

Lindberg and Ulmgren (1986) conducted laboratory trials on chemical grade lime in synthetic green liquor to investigate the effect of lime charge on the reaction rate. Figure 5 shows the change in causticizing degree over time for different charges of lime. One interpretation that Lindberg and Ulmgren have made is that a 5% overliming is sufficient to reach the desired causticizing degree within a certain time.

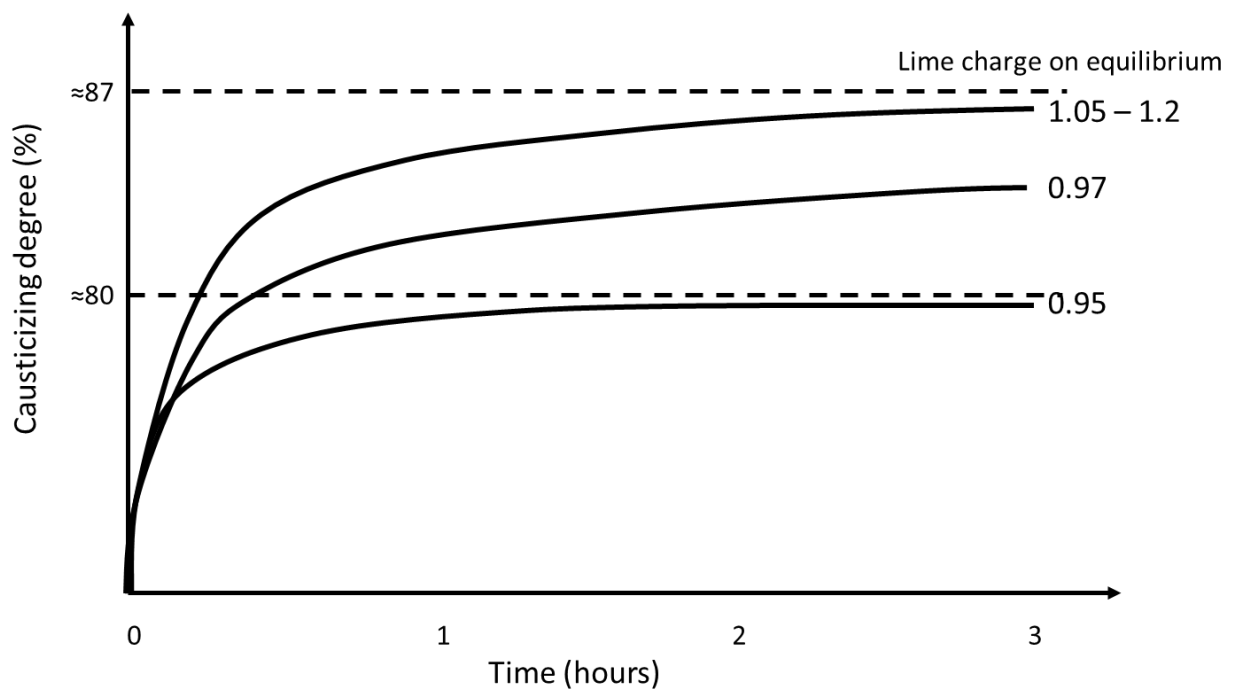


Figure 5: Causticizing degree as a function of time at different lime charges (as ratio of CaO needed to reach the equilibrium of the causticizing reaction, see Eq. 2 and 3).

Theliander (1987) suggests that in order to reach the desired chemical equilibrium at conditions normal in the industry, an excess lime of 1-2% is required, and this excess might need to be increased if the causticizing temperature is low, if the causticizing time is short or if the lime is hard burned. Theliander also found that a high-reactivity lime normally generates a lime mud that is difficult to separate, probably since a fast-reacting lime causes a high and rapid temperature increase that tears the lime mud particles apart.

The slaking reactivity and the causticizing reactivity (measured as change in hydroxide ion concentration in the solution during the initial 5 min in relation to the change after 180 min) increase almost linearly with increasing specific surface area, which depends on the degree of sintering. As mentioned in the paper by Theliander (1987), reactive lime with a high surface area, however, produces a lime mud that is hard to filter. The optimum reactivity is, thus, dependent on the filtering capacity and the residence time in the causticizing at each individual mill (Hanson, 1993). This is a fundamental conclusion that is not considered in daily operation.

It is generally accepted that charges of CaO that are too high impair filterability. Findings by Azgomi (2014) indicate that the reason for this is that the presence of uncausticized Ca(OH)_2 gives lower filterability and can be monitored by measuring the Zeta potential of the lime mud particles. The filterability is, however, also greatly affected by other conditions such as temperature and particle size distribution.

An excess of lime does not increase the overall production of alkali since the reaction is determined by the equilibrium in Eq. 2 and Eq. 3. Given that the lime is distributed between

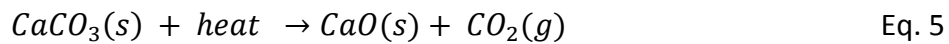
hard-burned and soft-burned fractions, which result in different particle size distributions, an increase in lime charge provides more of the soft-burned lime (smaller particles), which increases the reaction rate at the cost of higher lime consumption and higher particle concentration and impaired settling properties. This is in agreement with the findings by Lindberg and Ulmgren (1986).

4.2 Around and in the lime kiln

Guidelines for successful lime mud reburning have been similar for quite a long period of time. In 1980, it was recommended that lime mud should be somewhat thoroughly washed in order to suppress H₂S formation, but not too well washed in order to suppress dusting. The lime mud should have coarse particles for a high filtration rate and a low content of inerts to obtain good fuel economy. Finally, the lime mud should render evenly sized nodules of reburned lime as suggested by Carlhamn (1980).

4.2.1 On the calcination temperature

The purpose of the causticizing plant is to produce white liquor with a high and even quality. Therefore, the lime kiln must produce a reburned lime with a high and even quality. The calcination reaction is shown in Eq. 5.



Properties of the different calcium compounds present in the lime kiln and in the causticizing are given in Table 5.

Table 1: Physical properties of calcium compositions

	CaCO ₃	Ca(OH) ₂	CaO
Molar volume (m ³ /kmol)	0.037	0.033	0.017
Density (kg/m ³)	2 705	2 245	3 299
Molar weight (kg/kmol)	100.1	74.1	56.1
Structure	Calcitic (trigonal)	Hexagonal	Cubic

The calcination reaction is an endothermic equilibrium reaction, which is strongly influenced by the partial pressure of CO₂. The relationship between the partial pressure of CO₂ and the temperature is given in Eq. 6 (Baker, 1962).

$$\log P_{CO_2} = 7.079 - \frac{38\,000}{4.574 \times T} \quad \text{Eq. 6}$$

Mikulcic et al. (2012) have suggested a similar expression:

$$P_{CO_2} = 4.137 \times 10^{12} \exp\left(\frac{-20\,474}{T}\right) \quad \text{Eq. 7}$$

Both equations give very similar results in the industrially relevant range below 50% CO₂ and are shown in Figure 6.

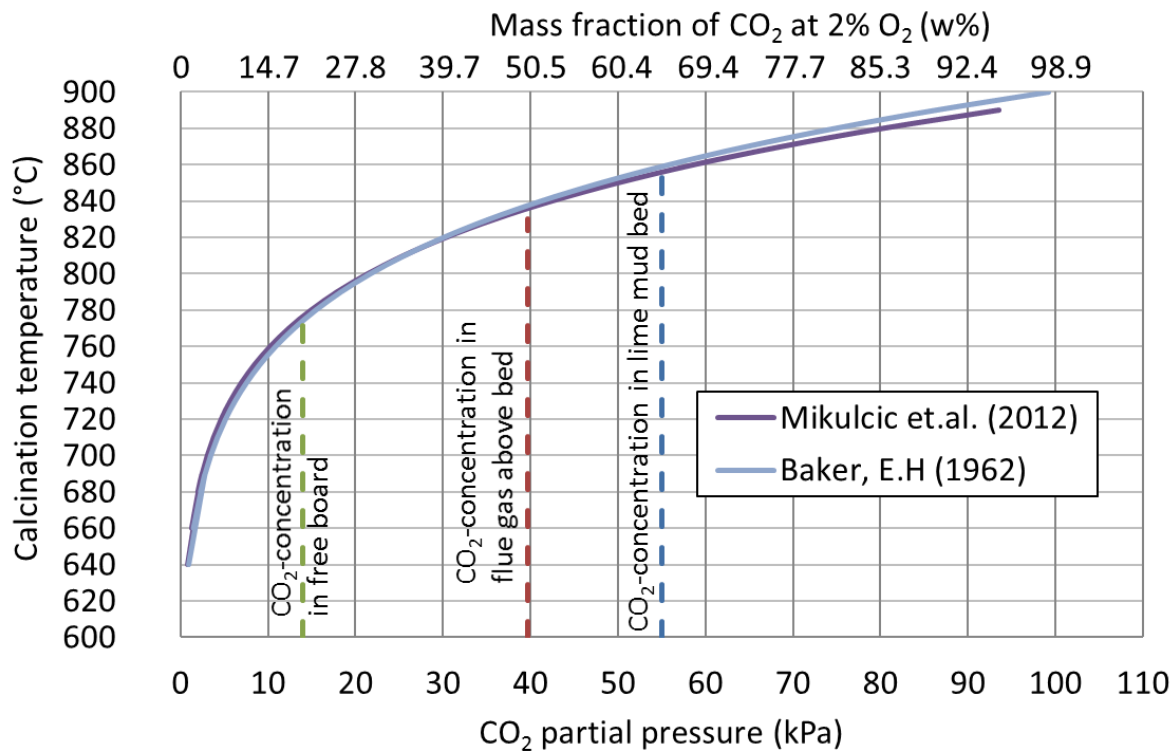


Figure 6: Calcination temperature as a function of CO₂. Approximate CO₂-concentrations in different parts of the kiln are indicated in the graph.

Tran et. al. (1993) investigated the reburning of lime mud using TGA/DTA equipment where the weight change and exotherm/enderm reactions are captured together with the temperature. It was found that pure CaCO₃ decomposes in pure air (close to zero kPa CO₂) at 640°C. This temperature is very close to the temperature in Figure 6. When heating industrial lime mud in the TGA/DTA equipment, however, two decomposition temperatures were monitored. The first, 330°C, at which the residual Ca(OH)₂ in the lime mud released H₂O and formed CaO. The second decomposition temperature occurred already at 600°C (calcination temperature). The lower calcination temperature for lime mud, compared to pure CaCO₃ was explained by the presence of Na₂SO₄ and Na₂CO₃ in the lime mud. When performing the TGA/DTA analyses on industrial lime mud in 80% N₂ + 20% CO₂, calcination occurred at about 820°C.

Lime mud reburning takes place in a heterogenous system with a mixture of gas and solids in the lime mud bed. The gas phase in the bed can be of a different composition than the gas phase in the flue gas above the bed. The consequence of this has been illustrated by Hanson and Theliander (1994) who performed experiments in a muffle furnace and found that industrial lime does not reach the maximum calcination degree until the material has reached 900°C, which implies that the bed has been saturated with CO₂.

Several efforts have been made to present a visual image of the processes taking place inside a lime kiln. One of them is a study by Tegehall et al. (2017), in which the software FLUENT was used to calculate the CO₂ concentration in different parts of the kiln. The results in Figure 7 show a CO₂ mass fraction of 50% around the bed, 20-25% in the flue gas and up to 70% in the

bed. Furthermore, the results show that the gas phase in a part of the bed close to the burner is nearly 100% CO₂.

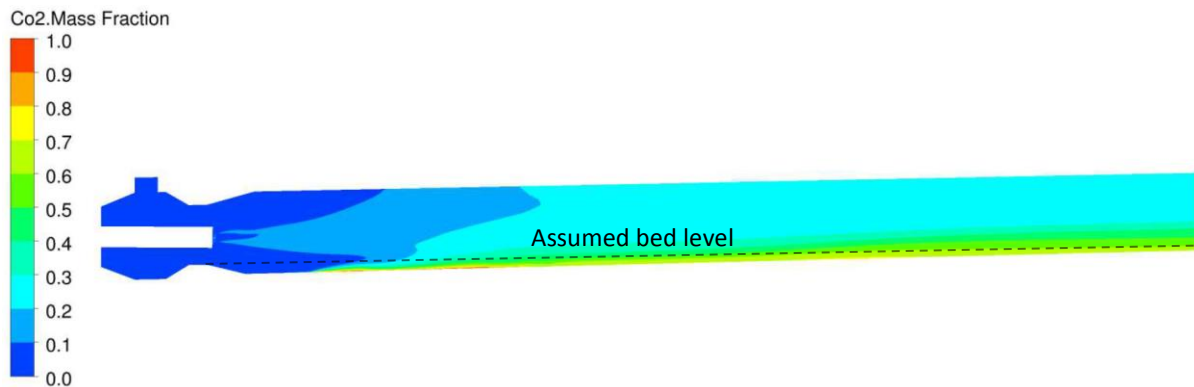


Figure 7: FLUENT simulation of the mass fraction of CO₂ in the flue gas and lime bed (Tegehall, Törmälä, & Jareman, 2017). The bed level is assumed to be determined by the height of the dam.

4.2.2 On the sintering and granulation of lime

Sintering is the reduction of the surface area of a solid material. The main driving force for the reduction of a specific surface area is the resulting reduction of free energy (Kuczynski, 1972).

Hanson (1993) investigated the effect of different atmospheres and different temperatures on the reburning and sintering of lime mud. 0.22 grams of lime mud was loaded in a 15 mm inner diameter cup, forming a bed with a depth of 3 mm. The lime mud had an initial specific surface area of 2.7 m²/g and was reburned at temperatures from 750-900°C in pure nitrogen. The specific surface area reached a maximum value of 5.5 m²/g at 900°C and 8 m²/g at 750°C within a few minutes. After a prolonged time, however, sintering of the reburned lime took place. After two hours, the surface area had decreased to 3.5 m²/g at 900°C and 6.5 m²/g at 750°C.

Hanson also shows that the sintering is pronounced even before calcination. Lime mud with a specific surface area of 3.7 m²/g was heated in 100% CO₂ at temperatures below the dissociation point (850°C). After sintering, the surface area of the lime mud decreased by 86% to 0.5 m²/g.

Another important observation in the work by Hanson (1993) is that sintering studies on calcined CaCO₃ p.a. are not directly applicable to the sintering of reburned lime. This was seen since the surface area of calcined CaCO₃ p.a. (CaO) increased at temperatures up to 900°C and began to decrease only when the temperature exceeded 900°C. When sintering calcined lime mud (reburned lime), however, the specific surface area decreased steadily as the temperature increased. For comparison, the calcination rates on the other hand were found to be very similar for CaCO₃ p.a. and industrial lime mud.

Hanson (1993) also found that the presence of SO₂, CO₂ and water vapor enhanced sintering by chemical reaction sintering, whereas the agglomeration of particles was likely caused by the presence of impurities. Lindblom et al. (1998) investigated the effect of various impurities on the degree of sintering and found that both Na₂CO₃ and Na₂SO₄ enhanced sintering, but Na₂CO₃ had a greater impact. The plausible explanation for this is the

difference in melting point between Na_2SO_4 and Na_2CO_3 and the subsequently enhanced heat transport.

The formation of nodules is a characteristic feature observed in lime kilns at Kraft pulp mills. It is commonly accepted that sodium and potassium salts melt at relatively low temperatures (300-900°C) and promote a tendency towards granulation. This has been explained in several studies: Tran et al. (1993) investigated the stickiness of the lime mud mixture as a function of sodium content and found that there seems to be a threshold around 1 w% sodium. Izhar (2004) has also investigated the role of sodium and other impurities in lime mud in the stickiness and deposition on a kiln wall. The findings are in line with the previous findings from Tran et al. (1993). Izhar's work has also shown that phosphorous (if not present as calcium phosphate) forms sticky deposits at temperatures above 600°C.

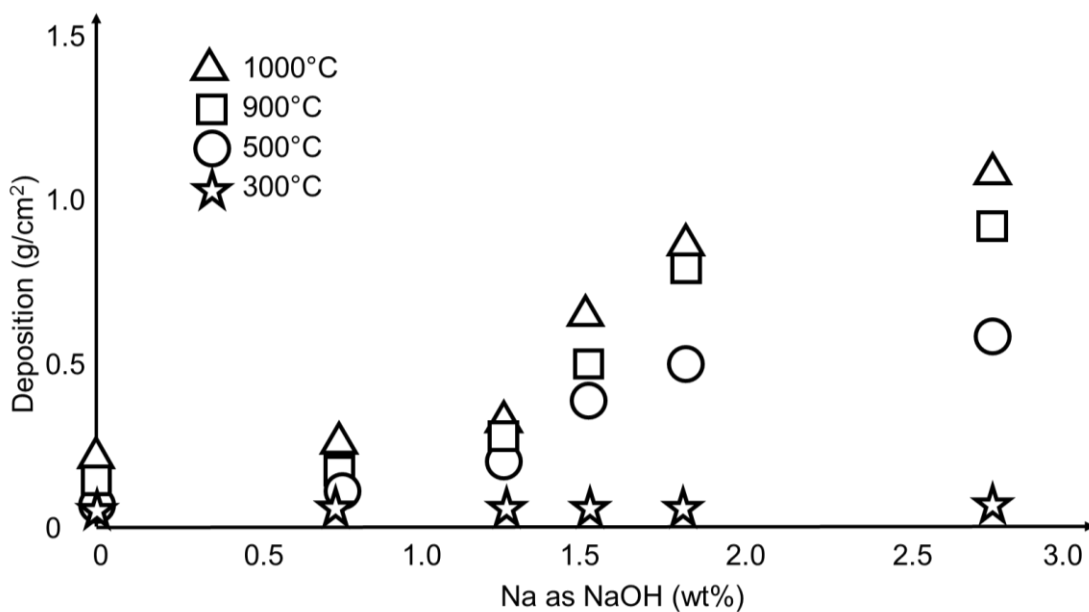


Figure 8: Material deposition depending on sodium in lime mud and temperature in kiln (Izhar, 2004)

Holmqvist and Jönsson (1993) conducted a study to establish an on-line testing method for determining the sintering degree of burned lime. They found that sintering makes the reburned lime denser and increases the E-modulus and the mechanical strength of the lime nodule. They observed that well-sintered lime does not cause any dusting problems. Holmqvist and Jönsson describe a measurement device in which lime nodules are collected and dropped on a hard, heavy plate. The sound is measured and correlated to the E-modulus, which is correlated to the degree of sintering. The mechanical strength of the reburned lime nodule was measured by pressing a steel tip into the lime nodule at a constant speed until the nodule broke. Holmqvist and Jönsson found a correlation of $R^2=0,96$ between the degree of sintering and the mechanical strength of the lime nodule.

Lindblom and Theliander (1998) found that there is a strong dependence between strength and nodule size in reburned lime from an industrial lime kiln; the smaller nodule the stronger it is. In a lab-study, pellets were made by compacting under different pressures.

Lindblom and Theliander (1998) found that there is strong dependence between strength and nodule size in reburned lime from an industrial lime kiln; the smaller the nodule the stronger it is. In a lab study, pellets were made by compacting under different pressures. Lindblom and Theliander found that at a constant compact pressure, the mechanical strength of the nodule increases with decreasing specific surface area, resulting in stronger lime nodules after sintering. If the lime mud is calcined prior to being pressed into pellets, the strength of the sintered pellets will be much higher than if the pellets had been formed from lime mud and then calcined and sintered. The reason for this is probably that the molar volume of CaO is much smaller than that of CaCO₃, cf. Table 5. This means that, after sintering, the particles that form a pellet are more densely packed when they are formed from reburned lime.

4.2.3 On the lime mud filter and process stability

Theliander (1988b) investigated the system around a lime kiln and found that all the process streams to the lime kiln must be stable in order to achieve uniform lime quality. The quality was found to vary extensively, and a large part of this variation could be correlated to the reburning temperature (recorded by the thermocouple situated under the burner). The main reason for the large variation in reburning temperature and the resulting variations in lime quality was found to be the process variation of the lime mud filter. Variations in the flow of lime mud to the lime kiln induce fluctuations in the reburning temperature. Thus, an even material flow from the filter to the kiln is of primary importance.

Wallbäcks et al. (2014) found that both the flow of lime mud to the kiln and the dryness of the lime mud from the filter is of importance for fuel demand and the reburning temperature, since drying consumes energy. The dry content after the filter and washing efficiency are influenced by how the filter is operated and by fluctuations in the quality of the lime mud from the causticizing, which in turn is dependent on the operation of the lime kiln and the presence of impurities in the lime mud that goes to the lime kiln.

4.2.4 Non-process elements

Non-process elements in the Kraft process are elements that do not take part in the desired chemistry in a given position in the process and have a negative impact on process performance. The sources of non-process elements are usually the raw wood material, makeup lime, the incoming process water and possibly the fuel in the lime kiln.

However, some elements added as process chemicals in one part of the process are carried over to another part of the process where they can create problems and, thus, act as non-process elements. (Keitaanniemi & Virkola 1982, Ulmgren, 1997). Examples of elements considered to be non-process elements are Ca, K, Mg, Mn, Si, Al, Cl and Fe. Calcium is an example of an element that is a process element in one part of the Kraft process (in the lime cycle in white liquor preparation) but a non-process element in other parts of the process (causing scaling in black liquor evaporation and in the fiber line).

Calcination of pure qualities of CaCO₃ (e.g. pure calcium carbonate or lime stone) and lime mud from the Kraft process is, in principle, the same reaction. Nevertheless, the structure and reactivity of reburned lime from pure qualities of CaCO₃ and the filterability of the formed lime mud after causticizing are very different from that of the reburned lime mud

(Hanson & Theliander, 1994). One major difference is the presence of non-process elements. Ulmgren (1997) investigated these elements thoroughly and discovered that silicon, which has rather high solubility in green liquor, precipitates together with calcium when the concentration of silicate ions exceeds 15 mmol/l. Ulmgren also found that the available CaO decreases by 6% by weight for every percent of Si in the lime. In similar manner, the available CaO decreases by 5% by weight for every percent of P in the lime.

Abson and Holman (1985) investigated the enrichment of non-process elements in the lime cycle and performed a laboratory study in which ash from hog fuel was added to lime mud. The mixture was then calcined at different temperatures. The reburned lime was slaked and causticized in a technical green liquor. The resulting lime mud was reburned again after removing the lime grits. This cycle was repeated 7 times until steady state was reached.

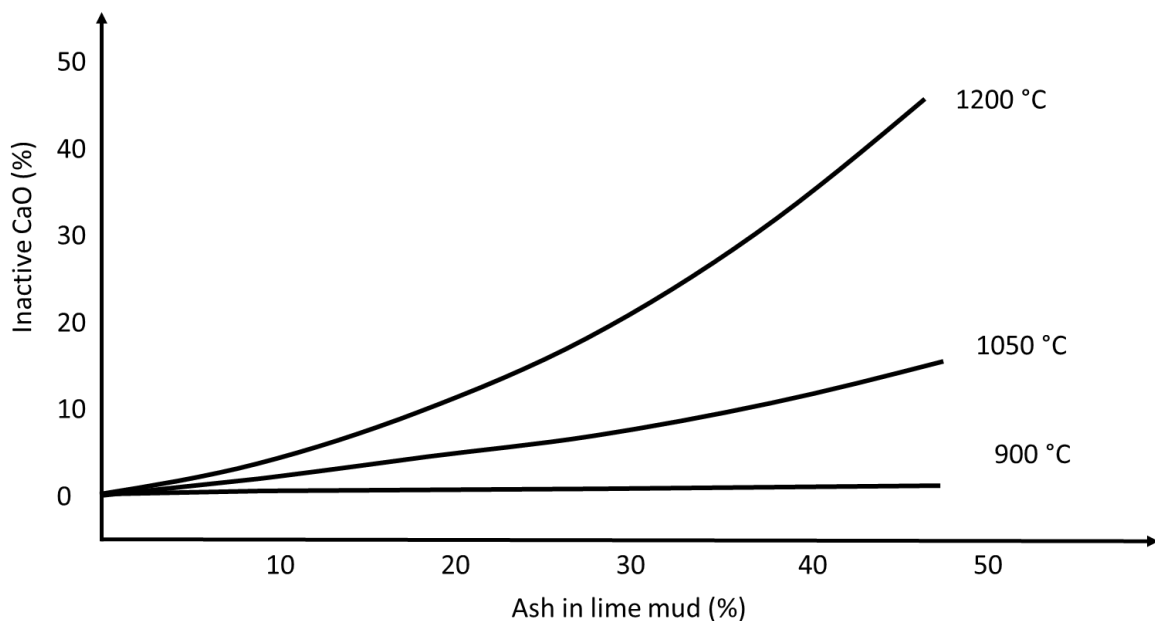


Figure 9: Inactive CaO as a function of ash content and temperature, based on data from Abson and Holman (1985).

Figure 9 shows that the inactive CaO is dependent on calcination temperature and is not noticeably influenced by the amount of non-process elements until the temperature exceeds 900°C. An explanation is that the CaO from the lime mud reacts with the contaminants in the ash at higher temperatures. The figure also shows that the higher the temperature is, the more pronounced the reaction/sintering rate is. An explanation could be that above 1150°C, Ca, K, Si, Fe, and Mg in the ash also form glass.

Lindberg and Ulmgren (1986) also investigated the effect of sintering. They found that the reactivity is determined by temperature and the amounts of Na, K, S, P, Mg, Al and Si, which generally increase the sintering tendency. This is indicated by the slaking time for calcined pure CaCO₃, which is virtually unaffected by a calcination temperature ranging from 900°C to 1600°C. This is in contrast to the slaking time for reburned industrial lime mud, which increases slightly with temperature when calcined below 1300°C and increases rapidly when calcined above 1300°C, since the impurities form compounds that lower the melting point.

The concentration of non-process elements in raw wood material, makeup lime and the incoming process water is relatively low. However, due to different solubility at different positions in the process, certain impurities can build up and reach concentrations at which process disturbances occur.

It is known that many metals, such as magnesium and manganese and phosphorus, accumulate in the lime cycle and that potassium and chloride accumulate in the alkali cycle, see Table 6.

Table 6: Accumulation of elements in the lime- and alkali cycle. Valid for Nordic conditions (Keitaanniemi & Virkola, 1982).

Accumulation factor Lime ¹				Accumulation factor Alkali ²			
Mg	7.5	Si	0.6	Mg	0.1	Si	0.5
Al	6.0	Na	0.4	Al	1.2	Na	-
Fe	5.4	K	0.2	Fe	0.6	K	11.6
Mn	2.3	Cl	0.04	Mn	0.3	Cl	3.7

1 Accumulation factor in lime cycle is the concentration in lime fed to lime kiln (kg/ADt) divided by the total amount introduced to the chemical recovery system (kg/ADt).

2 The accumulation factor in the alkali cycle is the concentration in white liquor (kg/ADt) divided by the total amount introduced the chemical recovery system (kg/ADt)

Silicon is to some extent accumulated in both the lime- and the alkali cycle. Normally however, the level of accumulation does not pose a problem for the operation of a mill operating at conditions corresponding to the ones at Nordic pulp mills.

However, notable accumulation can take place in mills with a high intake of silicon to the recovery area. This depends on the limited solubility of silica in white liquor (Ulmgren, 1997). Keitaanniemi and Virkola (1982) found that high silicon content is one reason for the low reactivity of lime, and a possible explanation is that the silicon compounds melt on the surface of the lime. The decrease in available CaO is especially pronounced when the lime temperature is higher than 1200°C. For the purpose of maintaining a high available amount of CaO in the reburned lime and high filtering capacity of the lime mud filter, those authors suggest that the silica content should be kept lower than 40 g/kg lime mud, and that the magnesium content should be kept below 11.5 g/kg lime mud.

The behavior of aluminum in the white liquor preparation process is also important for the performance of the recovery of chemicals in the Kraft process. High concentrations of aluminate ions, in combination with high silica concentrations, can cause severe scaling problems in the recovery area, especially in black liquor evaporators. Another important feature of aluminum is its interaction with magnesium ions. A high Mg to Al ratio promotes the formation of a sparingly soluble double salt containing Mg and Al (hydrotalcite) in the green liquor. Furthermore, the formation of hydrotalcite has been found to improve the filterability (and settling properties) of green liquor sludge, which is positive for the purge of non-process elements by means of green liquor sludge separation Ulmgren (1997).

5 Results and discussion

This chapter presents and comments on the results from this study. Section 5.1 deals with potential factors that could influence dusting in the hot end of a lime kiln. In section 5.2, a new procedure for calculating reburned lime production was used to investigate how process changes on the lime mud filter influence the performance of the lime kiln.

5.1 Dusting in the hot end of the lime kiln

It is common that mills occasionally have severe dusting in the hot end of lime kilns. The quality of the reburned lime produced most likely differs between dusting and clear periods, since conditions in the kiln are affected by the presence of dust. However, no information on the effect of a dusting lime kiln on the quality of the reburned lime could be found in the literature. This lack of information is the reason the present study was conducted.

5.1.1 Physical prerequisites for dust formation

A visual inspection of the hot end of a lime kiln reveals if the kiln is dusting or not. In Figure 10, it can clearly be seen that there is a difference in the appearance of a dusting and a clear kiln. The image of a dusting kiln shows that the dust consists of fine material dropped into the kiln from the portholes of the product cooler. It is also obvious in the image that dust does not enter from the portholes below but only from the coolers above, where the fine material falls due to gravity.



Figure 10: Left: Image of a dusting kiln. Right: Image of clear kiln

When fine material falls from the kiln top, an air flow that exceeds the terminal velocity of the dust particles hinders the material from settling and, instead, causes a dusty environment.

In order to estimate at which particle size the fine material causes dusting, the air velocity in the portholes can be compared with the terminal velocity at different particle diameters. Figure 11 describes the origin of the flue gas volume that exits the lime kiln no.2 in the Mönsterås mill. For a lime kiln production of 240 metric tons lime per day, a secondary air flow of around $10.9 \text{ m}^3/\text{s}$ is applied. If it is assumed that the secondary air enters evenly

distributed through the nine product coolers, the air velocity through each opening will be about 5 m/s.

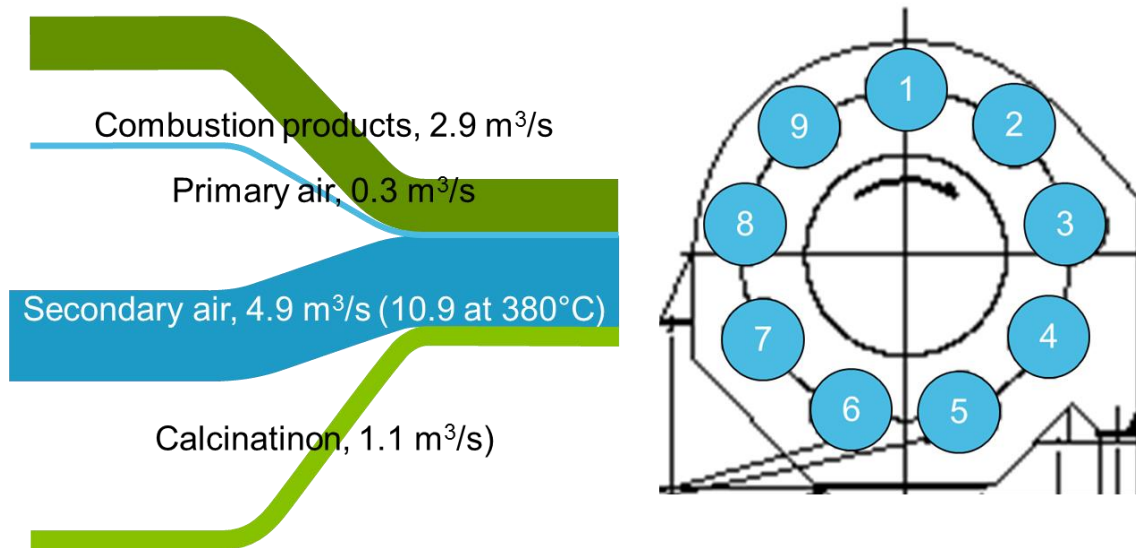


Figure 11: Origin of flue gas volume. All flows are recalculated as 20°C and 1 atm. The volume at 380°C is also given for secondary air.

Figure 12 (left) shows a calculation of terminal velocity as a function of particle diameter. The graph indicates that particles with a diameter of around 500 μm will contribute to the dusting at a flow velocity of 5 m/s. Figure 12 (right) gives the results obtained when dust collected from the interior of the kiln was analyzed for particle size distribution. The analysis showed that the major part of the particles had a diameter from 50 to 100 μm. Thus, the entrainment of fine particles is expected when fines in the range of 100 μm are present, but will hardly occur at all when the burned lime particles are larger than 1 mm; at such large diameters, the terminal velocity will exceed 9 m/s.

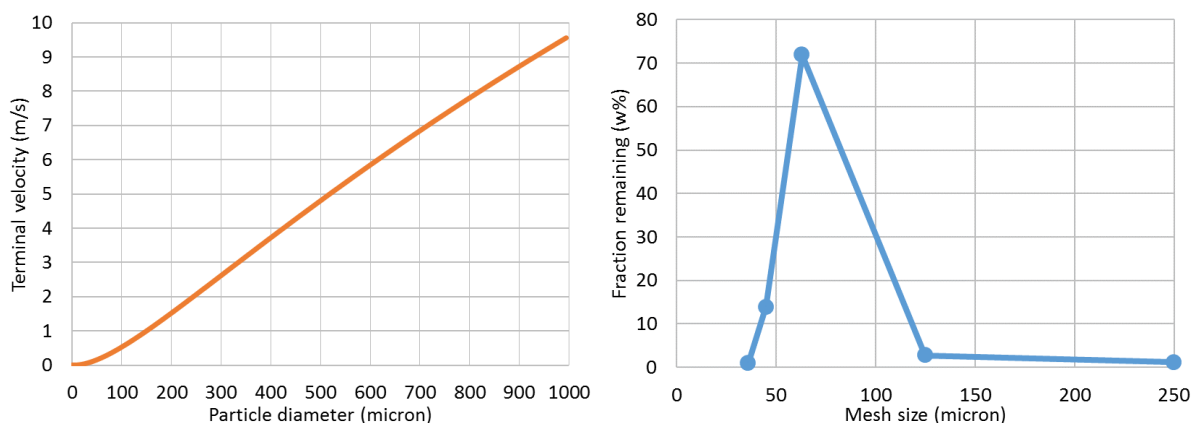


Figure 12: Left: Calculation of the terminal velocity of reburned lime particles as a function of particle diameter. Right: Particle size distribution of dust collected from the interior of the kiln.

5.1.2 Extent of granulation in the lime kiln

Samples of burned lime taken on different occasions were analyzed by sieving in order to quantify the influence of particle/granule size on the degree of dusting at the hot end of the lime kiln. Data from the sieving analyses, along with the corresponding temperatures measured, are shown in Table 7.

Table 7: Results from sieving of reburned lime connected during dusting or clear periods. Samples were collected during 2016. Temperature data from the pyrometer and the thermocouple are also included in the table.

Description	Date	Pyrometer °C	Thermocouple °C	<1 mm	10<x<15 mm
<i>Dusting</i>	26 March	889	802	49.7%	4.6%
<i>Dusting</i>	14 April	958	811	19.9%	13.6%
<i>Dusting</i>	15 April	894	736	12.7%	13.8%
<i>Dusting</i>	8 May	851	850	38.2%	10.0%
<i>Dusting</i>	5 Aug	943	895	16.4%	20.0%
<i>Little dusting</i>	18 May	1051	754	8.9%	14.2%
<i>Clear</i>	7 April	1148	878	3.2%	23.8%
<i>Clear</i>	8 April	1134	866	2.8%	22.7%
<i>Clear</i>	9 April	1145	850	2.5%	22.4%
<i>Clear</i>	30 June	1201	888	2.7%	22.2%
<i>Clear</i>	20 Nov	1175	803	1.1%	27.3%

The results in Table 7 show that the fines fraction in the reburned lime is much larger during dusting periods: In the dusting lime kiln, between 10 and 50% of the particles passed through a 1 mm sieve, whereas up to 10% of the particles were in the range of 10 to 15 mm. For the clear lime kiln, only a few percent passed through the 1 mm sieve, and 22-27% were between 10 and 15 mm. This may be an indication of a lower tendency for granulation in the lime kiln. However, another explanation could be that the formed granules either disintegrate or release fines material from their surfaces during the later stages in the lime kiln.

The temperature of the lime bed was measured with a pyrometer (optical measurement) that was mounted outside the kiln; there was a long distance between the sensor and the measured target. During dusting conditions, the pyrometer measured the temperature of the dusting particles rather than that of the surface of the lime bed. The thermocouple was mounted just under the burner and is influenced by the temperature of the surrounding gas to a larger extent than the pyrometer as can be seen in Figure 13. The temperature measured with the pyrometer was much lower at dusting conditions than at clear

conditions. However, the temperature measured with the thermocouple did not show any systematic difference between clear and dusting conditions, cf. Table 7. This indicates that the temperature conditions were about the same in the vicinity of the burner.

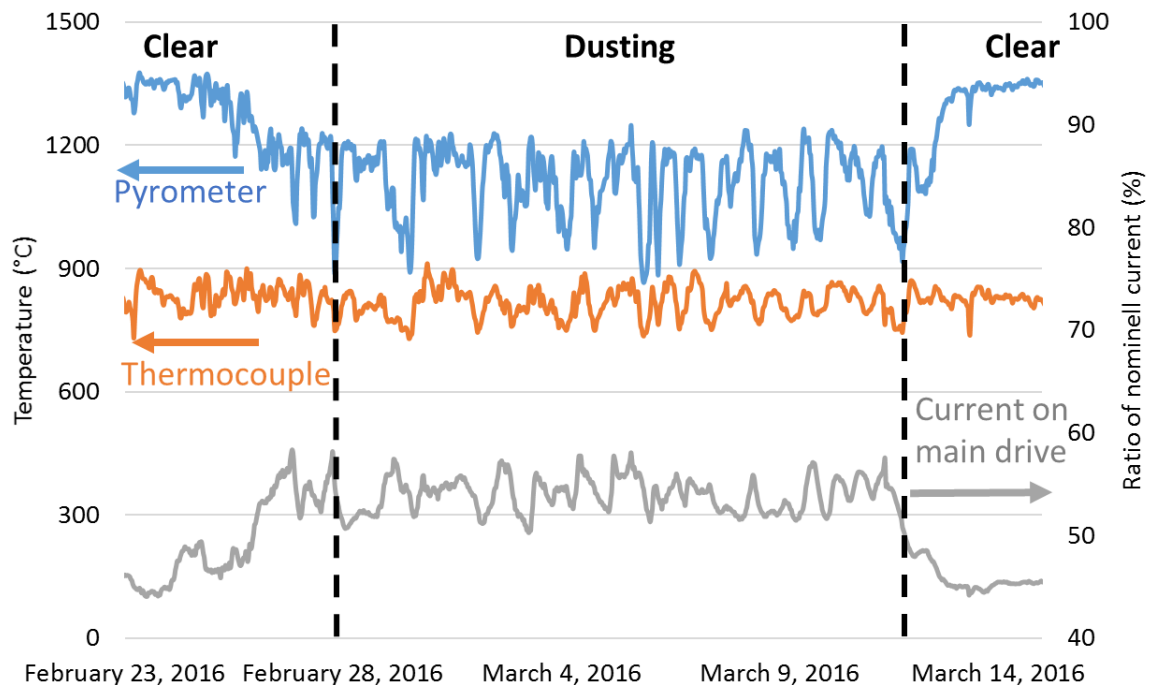


Figure 13: Transition from clear to dusting kiln around 28 Feb 2016 and back to clear around 11 March 2016. The pyrometer shows a temperature of around 1350°C when the kiln is clear and around 850°C when the kiln is dusting. The thermocouple is virtually unaffected by the dusting. The current on the main drive is commented in section 5.1.4.

5.1.3 Slaking and causticizing of reburned lime fractions from clear and dusting periods
 In order to investigate the effect a dusting lime kiln has on the white liquor preparation process, different fractions of burned lime (fines < 1mm and granules 10<x<15 mm) were slaked and causticized. The fractions were analyzed for available CaO, and an equal amount CaO was slaked and causticized in a synthetic green liquor in each experiment. The ionic strength and TTA in the synthetic green liquor were adjusted in order to resemble an industrial green liquor (see Paper I for details). Several setup procedures were used. These included both a lime charge far from the amounts needed to reach the chemical equilibrium (underliming) and lime charges corresponding to close to equilibrium.

A general observation was that the fines fraction, both from dusting periods and from clear periods, exhibited lower reaction rates than the granule fraction, illustrated in Figure 14.

On some occasions, the fines were so hard burned that the causticized white liquor did not reach a concentration of OH⁻ that equaled the one in the granules, even after 240 minutes. The lower reactivity of the fines fraction is most likely due to a higher degree of sintering in this fraction. This conclusion is based on observations that the specific surface area of the

fines fraction tended to be lower. In addition, the resulting lime mud particles obtained after causticizing were larger when the fines had been causticized since the hard-burned fines had withstood a higher separating force in the slaker than the soft-burned granules. The influence of degree of sintering on reactivity found in the present study is in accordance with earlier findings, cf. Hanson and Theliander (1994).

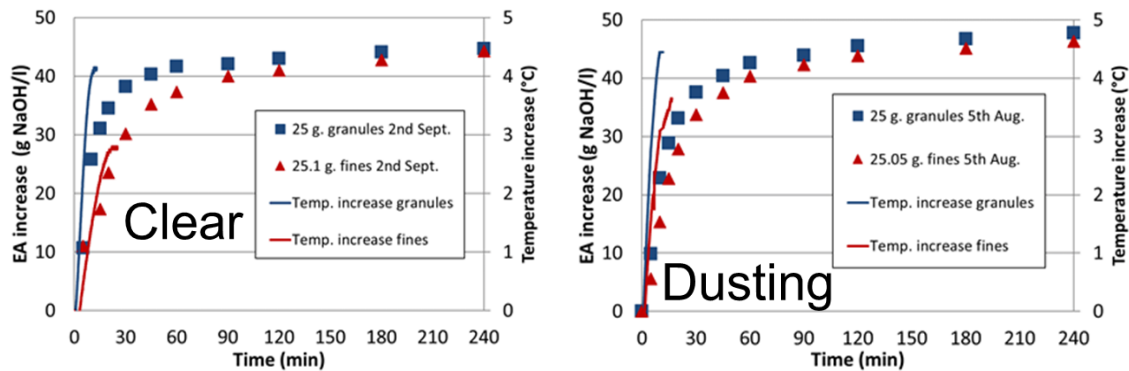


Figure 14: Causticizing - and temperature curves of fines and granules from a clear and dusting kiln.

The findings presented in this study have potential significant industrial relevance since the lime charge is regulated by the temperature measured in the slaker. The consequence in an industrial application is a substantial increase in the risk of overliming during dusting periods since the amount of fines is much larger. The fines release heat at a lower rate than the granules, which leads the dosing equipment to increase the lime charge until the desired temperature has been reached.

In order to further investigate the role of a high amount of fines in the lime on the rise of temperature during slaking, an additional study was conducted (unpublished results). Different amounts of granules and fines were added to 0.5 liters of synthetic green liquor. The different amounts were denoted by the percent of the calculated equilibrium, as shown in Table 4 using Equations 2-4.

The temperature rise was measured during the study, and the white liquor was sampled after 30 minutes. The time was chosen to resemble the time in the slaker. The results in Figure 15 show that there was a notable difference in heat released from fines compared to heat released by granules.

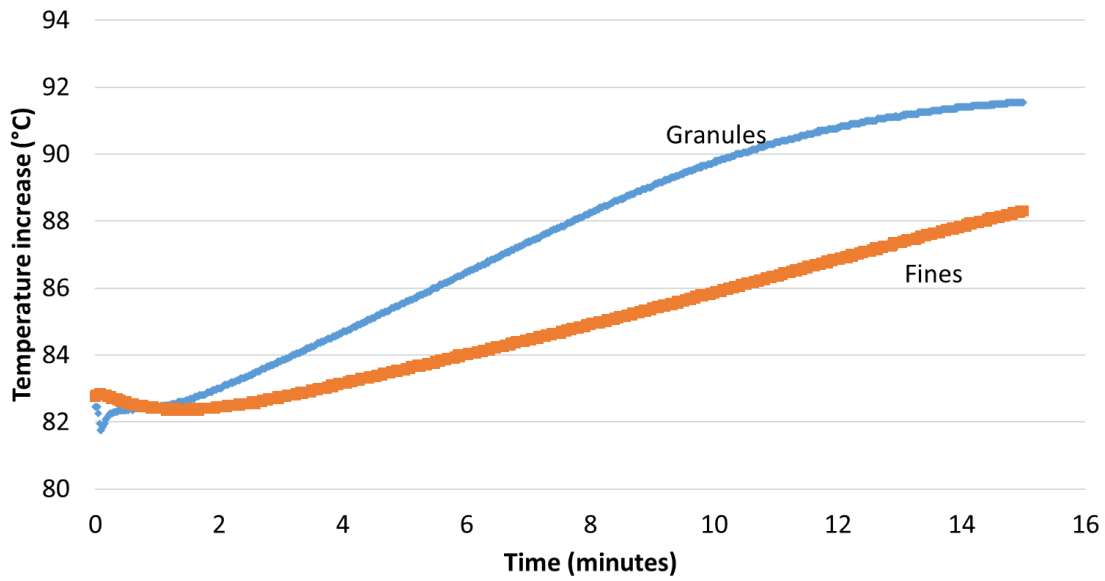


Figure 15: Temperature rise during slaking and causticizing of reburned lime in green liquor. The lime charge corresponds to the theoretical equilibrium in Equations 2-4.

The resulting concentration of effective alkali after 30 minutes is shown in Figure 16. This graph shows that the yield of effective alkali for the fines was lower than that of the granules. This is the same finding as in Figure 14, but Figure 16 shows that the findings are also valid for a lime charge and slaking temperature that are similar to those in an industrial application.

These findings suggest that if the lime charge is controlled by measuring the temperature in or directly after the slaker, the presence of fines increases the risk of overliming.

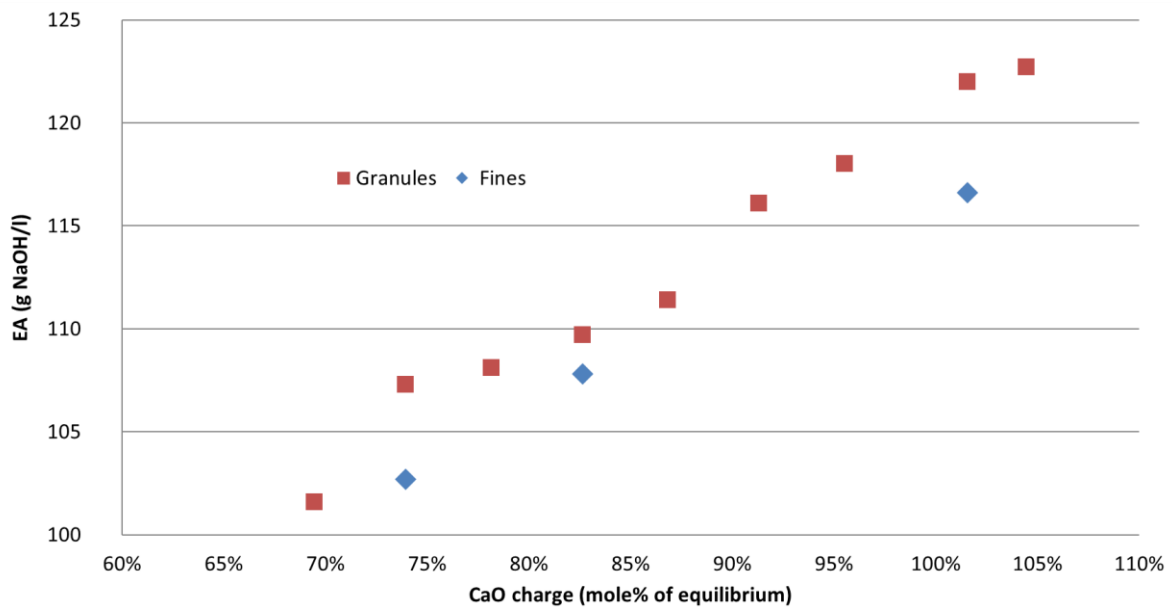


Figure 16: Effective alkali after 30 minutes depending on lime charge.

5.1.4 Cause of dusting

This section clarifies how different process conditions influence the presence of fines in the finished product.

Two observations can be made when assessing the process data from the investigated dusting and clear occasions.

The first observation is that during periods of dusting, shown by the decrease in temperature measured with the pyrometer in Figure 17, the power consumption that is required to rotate the kiln increases. Thus, the two signals are almost mirror images of each other (see also Figure 13). In Figure 17, the lime mud feed rate to the kiln and the fuel feed rate are stable in the shaded area. Nevertheless, the required power to rotate the kiln increased on the morning of 17 March 2017. During this period, there was no ring blocking the material from travelling forward. This is known since the kiln was stopped for inspection a couple of days later. During this stop, no ring was found. Thus, one can suspect that the build-up of material was due to dusting since the temperature measured with the thermocouple and the residual CaCO_3 had not been affected.

One possible explanation might be that the material inside the kiln was in the form of a powdery material. Such a material could possibly travel more slowly to the discharge due to its greater surface per unit of weight. This increase in surface could lead to greater friction that would counteract the gravitational force that transports the lime towards the discharge. Since the lime mud feed was the same, the residence time and the amount of material in the kiln was increased. As there was more material inside the kiln, more power was required to maintain the kiln at a given rotational speed.

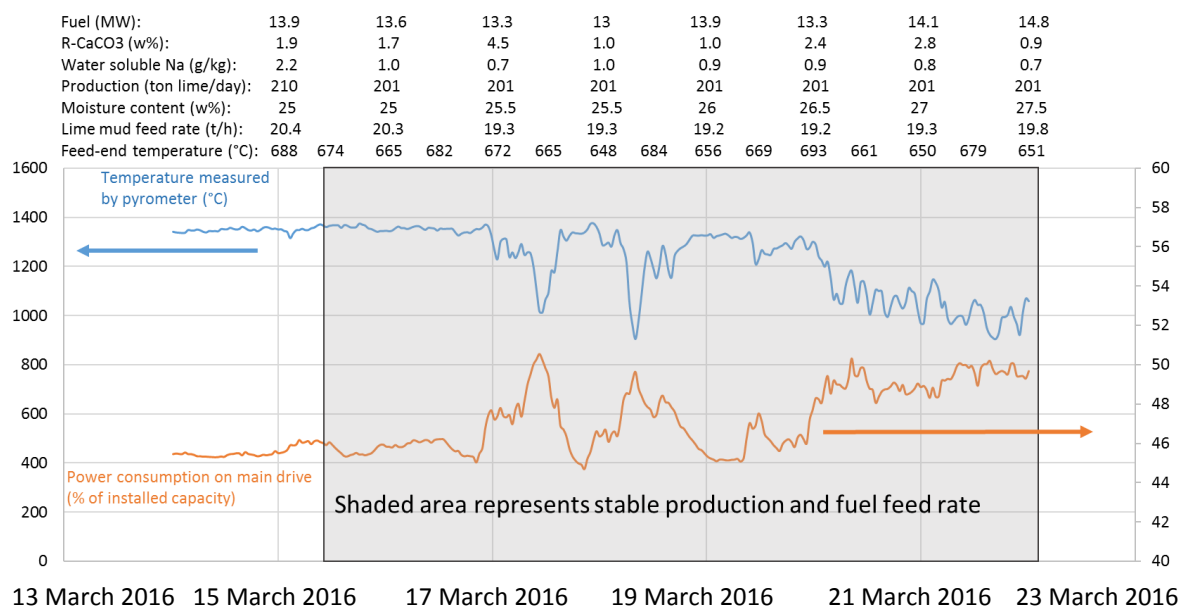


Figure 17: Increased power consumption during dusting. The production is given in metric tons of reburned lime/day.

The second observation, illustrated in Figure 18, is that the signal from the lime mud slurry flow rate oscillated more when the kiln was dusting than when the kiln was clear. The left-hand figure of Figure 18 shows the presumed transition from a clear kiln to a dusting kiln.

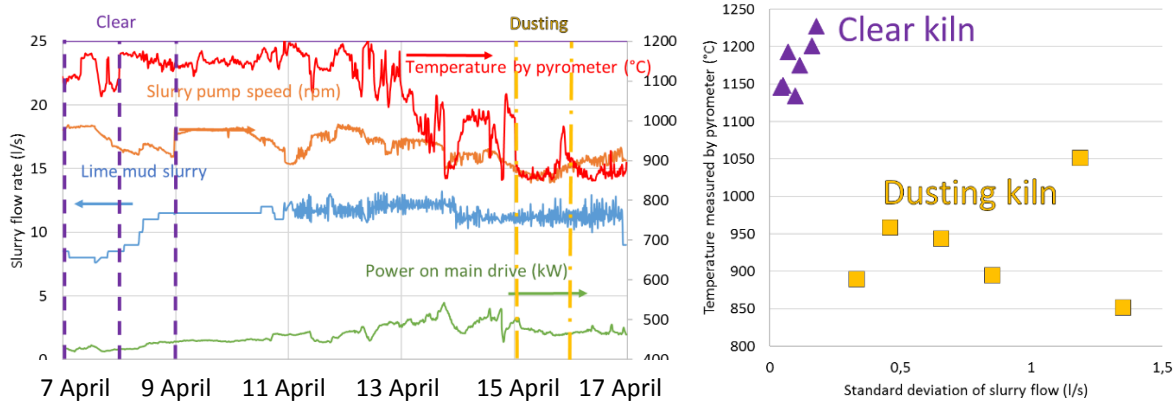


Figure 18: Left: Transition from clear to dusting kiln captured by the decrease in temperature measured with the pyrometer together with the increased demand for power to rotate the kiln and the signal from the lime mud slurry flow rate. The dashed lines represent physical samples from Table 7. Right: The temperature measured with the pyrometer at different standard deviations of lime mud slurry flow rate. Trend from 7 April 2015 to 17 April 2015.

The transition is represented by the decrease in lime temperature, measured with the pyrometer, and the increase in power required to rotate the kiln. One can also see that both signals from the lime mud slurry feed rate and the lime mud slurry pump oscillated more when the kiln was dusting than when the kiln was clear. In the right-hand graph of Figure 18, it is shown that this observation seems consistent for all clear and dusting periods that were investigated.

No in-depth insight into the cause and effect of the oscillations has been found. However, it can be generally assumed that the dusting in the kiln might be affected by the processes upstream from the kiln and not only by the operation of the kiln itself.

5.1.4.1 Presence of non-process elements

In section 5.1.1 it was described that dusting is caused by the particle size of the reburned lime. In section 4.2.2 it was concluded from earlier investigations that the presence of sodium is widely accepted as the determining factor for explaining the formation of nodules in the lime kiln. Therefore, it was natural to quantify the difference in sodium content in the lime mud, reburned lime and the ESP dust.

The results in Table 8 and Table 9 show that the sodium content was *not* lower in the lime mud from the dusting kiln. In fact, the average sodium content was slightly higher than that of a clear kiln. This is unexpected since it is commonly accepted that the presence of sufficient amounts of sodium is determining for the sticky behavior that e.g. influences the formation of deposits (c.f. section 4.2.2). P, Mg and Si had higher averaged concentrations in the lime mud from the dusting kiln, but the difference was not significant in terms of standard deviation. Table 8 and Table 9 also show the enrichment factor of each element calculated as the ratio between the concentration of an element normalized with calcium content in the lime mud, cf. Paper I.

The notable difference between a dusting and clear kiln was that the sodium, potassium and sulfur is more enriched in the ESP from a dusting lime kiln.

Table 8: Averaged concentrations of chemical elements and enrichment factors from 5 dusting occasions dating from 26 March 2015 to 5 August 2015. The standard deviation is given within parantheses in the table.

	Lime mud Content (g/kg)		ESP Content (g/kg)		Lime Content (g/kg)		ESP Enrichment (-)		Lime Enrichment (-)	
Na	8.5	(0.7)	21.4	(4.0)	13.2	(0.9)	2.8	(0.5)	1.0	(0.0)
P	10.7	(2.0)	17.4	(4.2)	16.5	(4.0)	1.8	(0.2)	1.0	(0.0)
Mg	9.6	(0.8)	9.7	(1.1)	14.8	(1.5)	1.1	(0.0)	1.0	(0.0)
Al	0.5	(0.0)	0.5	(0.1)	0.8	(0.1)	1.1	(0.1)	1.0	(0.1)
Fe	0.2	(0.0)	0.2	(0.0)	0.4	(0.1)	1.0	(0.1)	0.9	(0.0)
Si	1.7	(0.1)	2.1	(0.3)	3.1	(0.3)	1.4	(0.1)	1.2	(0.0)
K	0.2	(0.0)	2.6	(0.3)	0.6	(0.1)	15.8	(4.5)	2.3	(0.7)
Zn	0.4	(0.1)	0.5	(0.1)	0.7	(0.1)	1.3	(0.1)	1.0	(0.0)
S	0.6	(0.2)	8.1	(3.2)	0.5	(1.1)	16.9	(8.3)	0.9	(2.1)
C	106.0	(2.5)	100.2	(1.5)	0.2	(0.4)	1.0	(0.1)	0.0	(0.0)

Table 9: Averaged concentrations of chemical elements and enrichment factors during 5 clear occasions dating from 7 April 2015 to 20 November 2015. The standard deviation is given within parantheses in the table.

	Lime mud Content (g/kg)		ESP Content (g/kg)		Lime Content (g/kg)		ESP Enrichment (-)		Lime Enrichment (-)	
Na	7.7	(2.1)	13.6	(1.6)	13.0	(1.0)	1.7	(0.4)	1.0	(0.1)
P	8.7	(3.7)	15.2	(3.8)	14.4	(3.6)	1.7	(0.1)	1.0	(0.0)
Mg	7.4	(2.8)	9.2	(0.9)	13.8	(1.1)	1.2	(0.3)	1.1	(0.2)
Al	0.4	(0.1)	0.5	(0.0)	0.6	(0.3)	1.1	(0.1)	0.9	(0.4)
Fe	0.2	(0.0)	0.2	(0.0)	0.3	(0.1)	1.0	(0.2)	1.0	(0.4)
Si	1.5	(0.4)	2.1	(0.3)	2.7	(0.2)	1.3	(0.1)	1.0	(0.1)
K	0.2	(0.1)	0.9	(0.6)	0.5	(0.2)	5.5	(4.8)	1.7	(0.9)
Zn	0.3	(0.2)	0.3	(0.1)	0.5	(0.3)	1.0	(0.2)	0.9	(0.3)
S	0.6	(0.3)	9.2	(4.6)	0.7	(1.0)	14.9	(6.7)	1.1	(2.0)
C	105.9	(2.0)	100.1	(2.8)	0.6	(0.9)	0.9	(0.2)	0.0	(0.0)

To better understand the variations in the elements in Table 8 and Table 9, analyses of the chemical elements in reburned lime from 117 samples were compared. A table of correlations was drawn up and is shown in Figure 19. The correlations were made by plotting the data points for each element against each other. It can be found in Figure 19 that there is a large positive correlation between Mg and P and between Al and Fe. There was also a slight correlation between Si and Mg and between Si and P. The data points of the correlations between Al and Mg or Al and Si seem to be grouped into two different positive correlations.

The tendency for a higher concentration on non-process elements in a dusting lime kiln (Tables 8 and 9) indicates that the quality of the lime could be an influencing factor. However, the scattered data makes it difficult to draw any certain conclusions. In this context, it is of interest to also mention the fresh lime intake, which is made in order to

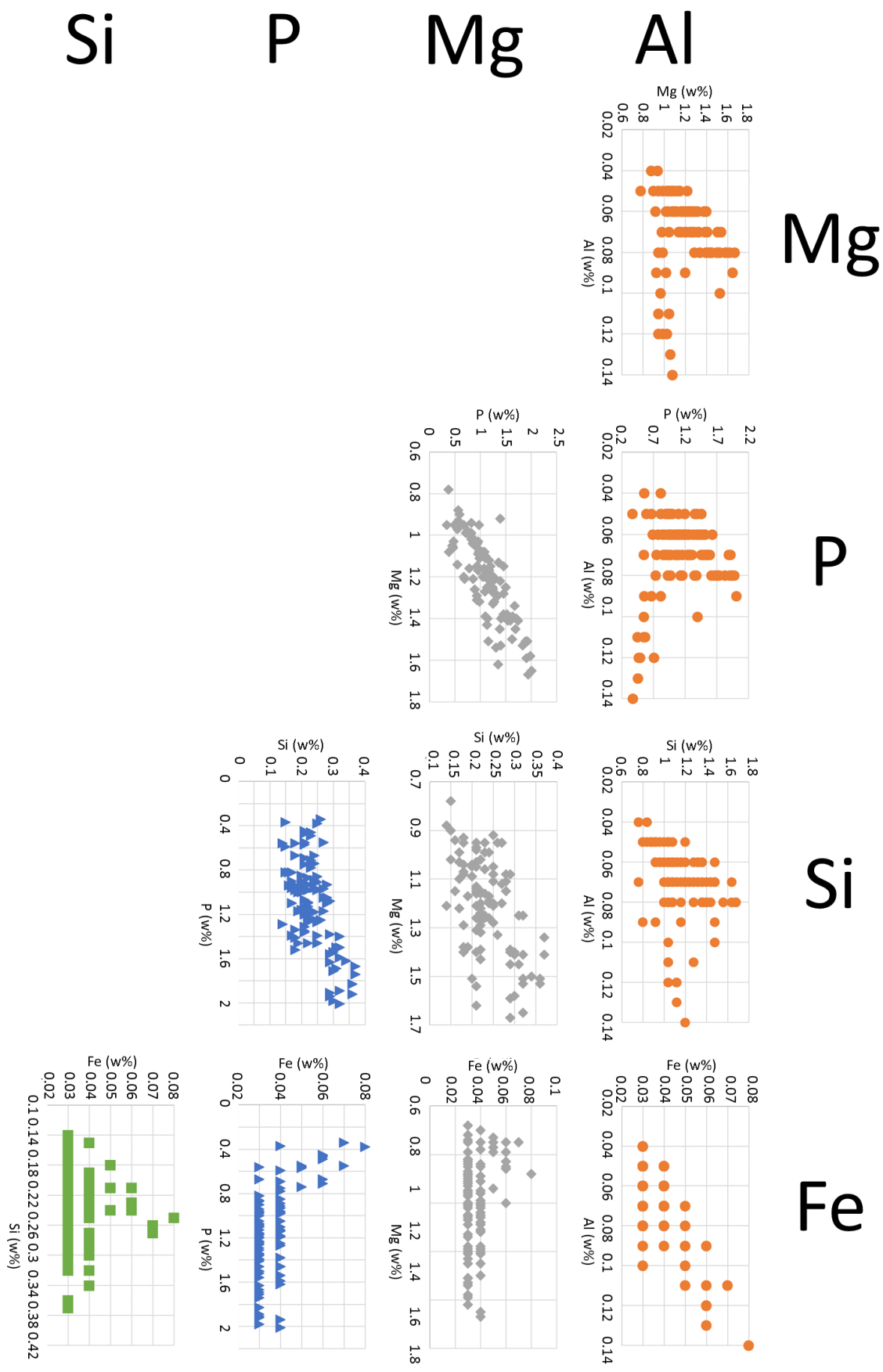


Figure 19: Matrix of correlations of chemical elements.

contain or suppress the concentration of certain non-process elements. Jullander (1982) has estimated the optimal fresh lime intake with respect to energy demand in the lime cycle to 9-14 kg/ADt. This is comparable to the 14 kg of fresh lime per ADt that was used in the Mönsterås mill.

The water-soluble sodium was measured separately. However, no notable difference in water-soluble or total sodium between a dusting and a clear kiln was found. Nevertheless, it is well accepted that sodium promotes nodule formation in a lime kiln. Boniface et al. (1968) have found that water-soluble sodium should be 0.15-0.52% in the lime mud. Therefore, a full-scale mill trial was conducted in which the washing water on the lime mud filter was shut off for 48 hours. The trial was conducted during a period when the kiln was dusting.

The water was shut off on 17 August 2015 at 09:11. The water-soluble sodium increased from 0.07 to 0.2%, and the moisture content of the lime mud after the lime mud filter decreased from 29% to 26% (Figure 20).

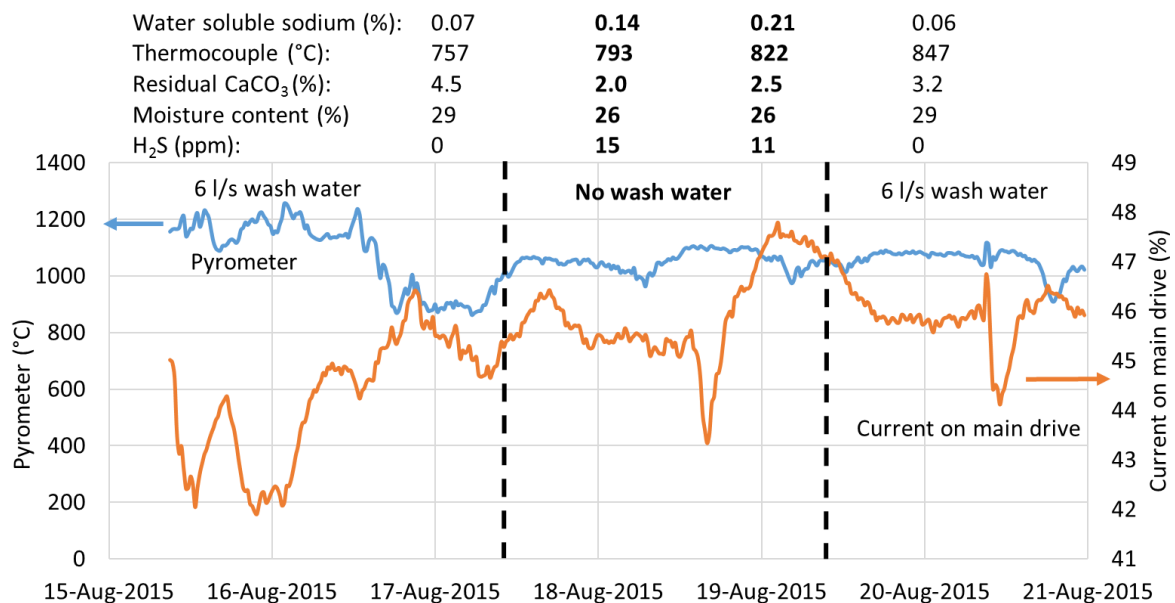


Figure 20: Operation data from mill trial when wash water was shut off.

Due to the lower moisture content of the lime mud, the temperature of the flue gas after the flash dryer increased (not shown). The residual CaCO₃ decreased during the trial. A possible explanation is that since the lime mud had a greater dryness after the lime mud filter, the vaporation- and heating zone was shorter, leading to the calcination zone to come sooner in the kiln. This leads to a longer sintering zone and thus a more hard burned lime with a lower residual carbonate content.

As seen in Figure 21, however, no clear improvement regarding the dusting in the lime kiln could be observed even after 24 hours.

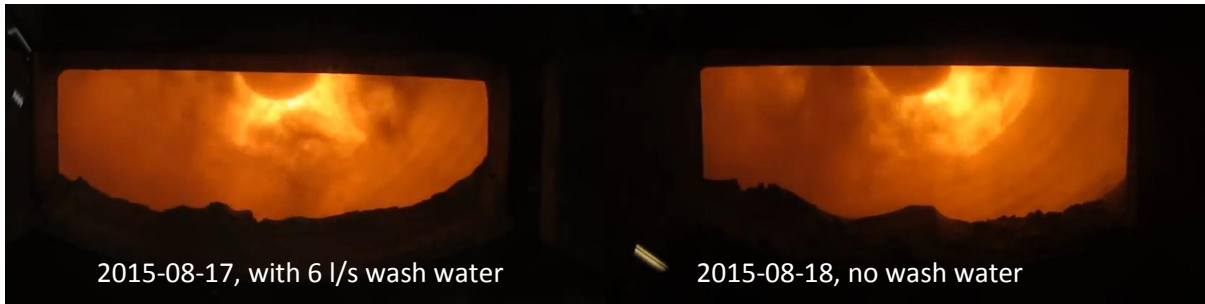


Figure 21 Burner end of a dusting kiln when the lime mud had been washed with 6 l/s on 17 August 2015 and without washing 18 August 2015.

One finding of this study is that, despite the already known and commonly accepted relationship between sodium and adhesion between particles, the sodium content in lime mud does not explain the dusting in the burner zone of the kiln.

5.1.4.2 Presence of fine particles

In three full-scale mill trials, ESP-dust was completely removed from the kiln by vacuuming it onto a truck. The first trial took place during a dusting period on 17 June 2015 from 08:30 to 15:30. The amount of ESP dust vacuumed was noted by the scale of the truck. The result, shown in Figure 22, was that the load on the ESP was very unstable compared to the dry solids feed rate from the lime mud filter. The feed rate of ESP varied by 0.6 t DS/h, whereas the lime mud from the filter varied around 0.1 t DS/h measured with an on-line band scale and an on-line moisture content measurement device.

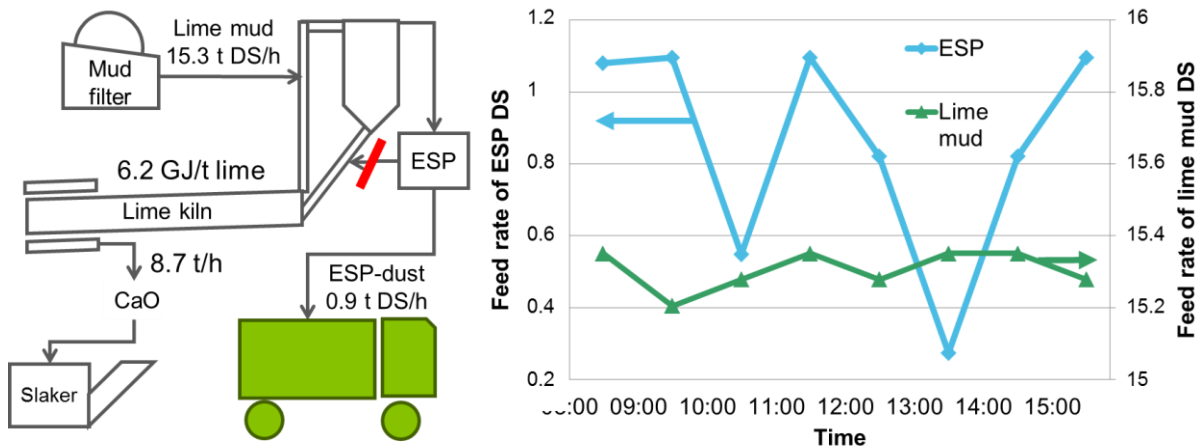


Figure 22: System of removing ESP dust and the result of weighting the vacuumed material loaded onto a truck. Unit in the diagram is metric tons DS/hour. Data are from the first trial on 17 June 2015 from 08:30 to 15:30.

The result of the first trial on a dusting kiln was evaluated by visual inspection where it could be seen that the kiln became clearer after all ESP dust had been evacuated for 7 hours (Figure 23). The results were somewhat unexpected, since sodium is enriched in the ESP-dust (Table 8 and 9) and is commonly accepted to play an important part in the nodulization process. Removing sodium from the lime mud feed to the kiln could therefore be expected to impair granulation and provoking dusting in the burner zone.



Figure 23: Before removal of ESP dust (left) and after removal of ESP dust (right) from 17 June 2015.

The result of the second trial on a clear kiln performed on 30 June 2015 was also evaluated by visual inspection. No significant change could be seen since the kiln was already clear and no negative effects were noted (Figure 24).



Figure 24: Before removal of ESP dust (left) and after removal of ESP dust (right) from 30 June 2015.

A third trial was performed on 5 August 2015 on a dusting kiln. In this trial, the reburned lime from the discharge was sampled before and after the removal of ESP dust.

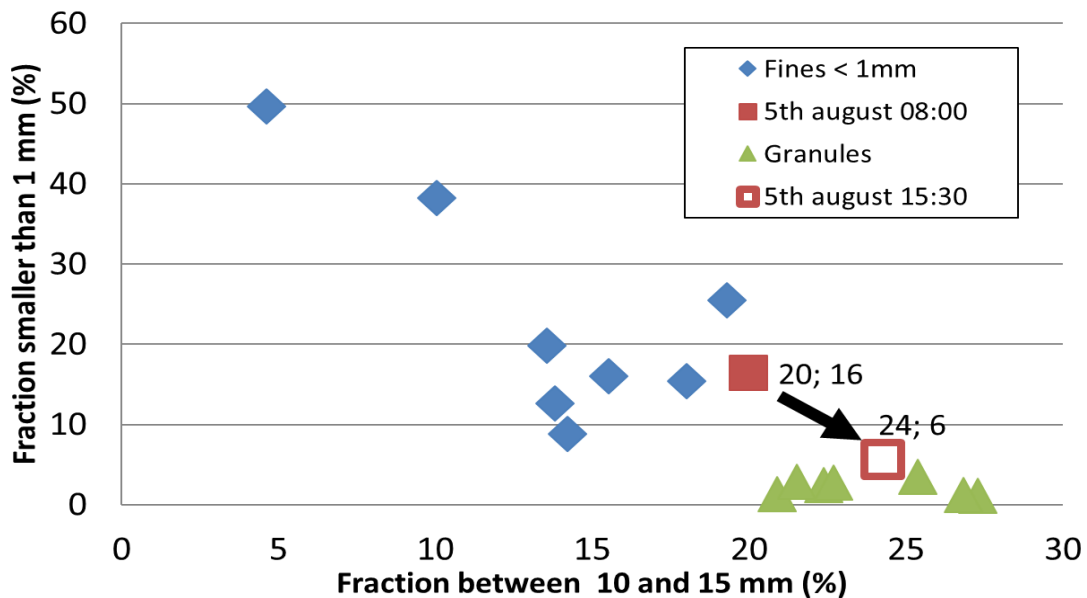


Figure 25: Sieving results showing the effect of removing ESP dust from the lime cycle on the 5 August 2015. For comparison, data from other dusting clear periods are included. The fraction of granules is plotted on the x-axis and the fraction of fines is plotted on the y-axis.

The results in Figure 25 show that the weight fraction of the fines decreased from 16% before the removal of ESP dust to 6% after the ESP dust had been removed during 7.5 hours.

A possible explanation for this is that the ESP dust had agglomerated before calcination due to its smaller size (Pietsch, 2008) and, thereby, formed weaker agglomerates (Lindblom & Theliander, 1998) that are more likely to generate fine material.

The results from this section suggest that the varying load on ESP could have an influence on the presence of fine material and, thus, the dusting at the hot end of the kiln. The mechanisms are not completely revealed, but a possible explanation could be the abrasion of agglomerates with lower mechanical durability.

5.2 Process stability in the kiln

As pointed out in Section 4.2.3, the stability of the performance of a lime kiln and causticizing is strongly dependent on a stable flow from the lime mud filter. In the present work, a new procedure for calculating reburned lime production is proposed. This calculation requires measurements of mass flow, moisture content, and the carbon content of lime mud and reburned lime. Södra Cell in Mönsterås invested in a band scale, an NIR detector, and a carbon content analyzer to set up this new calculation procedure and to achieve better control of some of the process parameters affecting reburned lime production. After the band scale and the NIR moisture detector had been installed, fluctuations in lime-mud production and moisture content were noted, and a more detailed study of the reasons for, and consequences of, these fluctuations was conducted.

5.2.1 Variations in lime mud filter and feed-end temperature

Based on the results in Figure 22, which suggest that the load of the ESP dust is unstable during dusting, it is proposed that process stability in the kiln is important for a stable load on ESP and for the dusting in the burner zone.

Measurements of the moisture content of the lime mud and the weight of the dewatered lime mud were compared with a dynamic simulation of the temperature profile in the kiln. It was found that the effects of minor temperature variations were captured by the simulation. The temperature variations can be explained by the movement of the water jet on the lime mud filter. The purpose of the water jet is to remove the lime mud precoat on the filter (Figure 26). The simulation also showed that the impact of these temperature fluctuations induced by the water jet were minor and did not influence the long-term stability of the kiln. This

finding means that there was no need for corrective actions by the operators, which was a common experience at the mill.

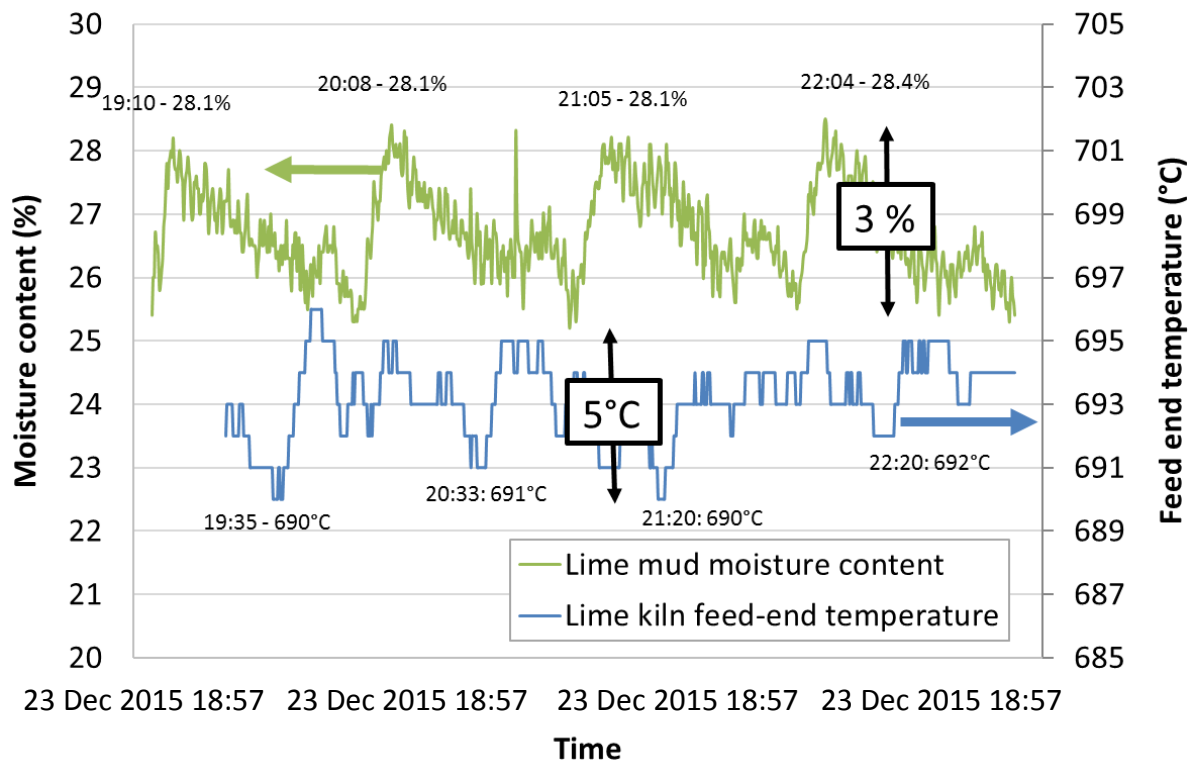


Figure 26: Effect of lime mud moisture content variations on lime kiln feed-end temperature during stable fuel feed (100% heating oil at 32.5 MW) and production rate (415 metric tons/day). The measurements were performed on kiln no.1.

The newly installed equipment for measuring the moisture content and weight of the dewatered lime mud also helped in noting a sudden and largely unintended increase in the feed rate of lime-mud dry substance to the kiln. As seen in Figure 27, the increased feed rate, induced by process disturbances in the filter, lowered the temperature at the feed-end of the kiln for around 90 minutes.

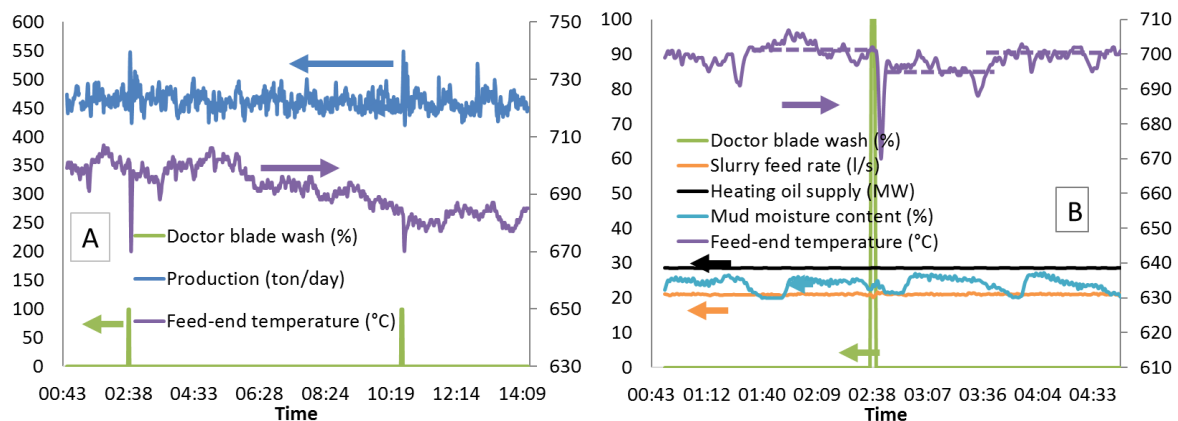


Figure 27: Left: Increased production (i.e. lime mud feed rate) and lowered temperature due to washing of doctor blade at around 02:38 and 10:19. Right: Temperature decrease by 5°C for a 1-hour duration following a sudden increase in lime mud feed rate. The measurements were performed on kiln no.1.

Interestingly, the simulation could only explain about 7°C of the 30°C temperature drop that occurs at 02:38 in Figure 27. The reason for this is that the simulation assumes that all lime mud is carried over to the cyclone and none is fed directly into the kiln. A possible explanation could, therefore, be that the marked increase in lime mud on the filter leads to that part of the lime mud not being carried over to the cyclone. Instead, the lime mud fell directly into the kiln without being properly dried first. This exhibits the practical use of both the measurement setup and the simulation tool. The measurement was necessary for detecting the increase in lime mud on the filter, and the simulation was necessary for identifying the possible cause of lime mud not being properly dried. As seen in the right-hand side of Figure 27, the feed-end temperature was lower by 5°C for a 1-hour duration, which would potentially move the calcination zone in the kiln.

If the kiln operates at stable conditions and the temperature in the feed-end suddenly drops, the lime mud will travel further into the kiln before being completely dried and heated up. Therefore, there will be less time for completing the calcination and the final heating of the lime. Upon noting that the temperature in the feed-end deviates from what is desirable for a stable lime kiln, a natural response is to increase the feed rate of the fuel with a subsequent rise in temperature when the cooling disturbance is no longer present. When exploring this phenomenon, the following pattern was found; every eight hours, the feed-end temperature dropped between 10°C and 30°C. When investigating the processes around the filter, it was found that the only operation with the same periodicity was the washing of the back side (facing the filter) doctor blade from stuck lime mud. This washing water raised the level in the vat, which enabled the filter to take up more lime mud on the filter cloth.

An action taken by the mill personnel after this regular process disturbance had been discovered was to cover the back of the doctor blade with a non-stick material, turn off the washing water, and, thus, remove the disturbance.

The results from this section show that the hourly process variations induced by the water jet for lime mud precoat removal on the lime mud filter are not likely the cause of any notable process disturbances that can explain the varying load on ESP. There were, however, significant disturbances that were probably caused by lime mud not being carried into the flash dryer. This lime mud would have fallen directly into the kiln before being properly dried. This could cause a lasting change in the feed-end temperature and could, thus, also affect the ability of the flue gas to carry lime mud into the flash dryer.

5.2.2 Effects of shutting off the dilution water to the vat of the lime mud filter

During this trial, water to the vat used to maintain a steady level was shut off (Figure 28). The purpose of the trial was to investigate how the water affected the lime mud moisture content and lime mud feed rate after the filter. The water that is added for level control was suspected to cause a variation in the dilution of the slurry and a varying dry content of lime-mud dry solids in the vat.

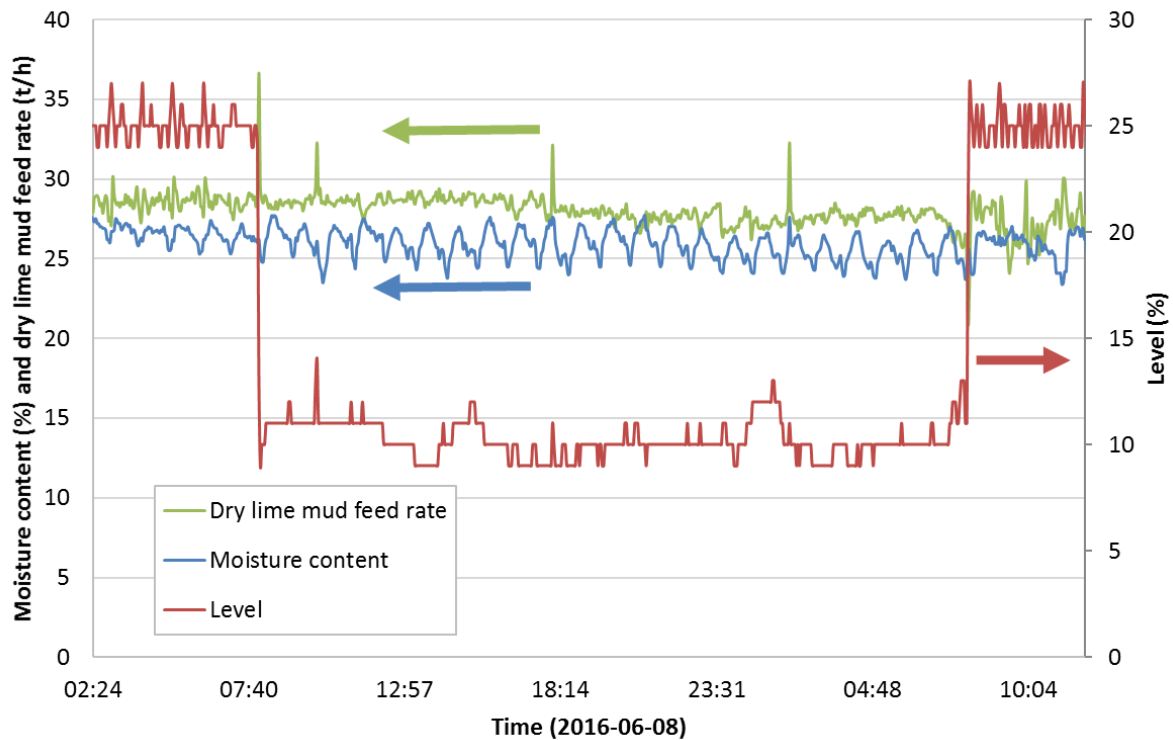


Figure 28: Effects of shutting off the dilution water to the vat of the lime mud filter. The fuel supply and lime mud feed rate after the filter were constant (32.3 MW and 38.8 metric tons/hour). The vacuum went from -60 kPa to -54 kPa. The distinct spikes in the dry lime-mud feed rate are from the washing sequence of the doctor blade.

However, the results show that the standard deviation in moisture content actually increased from 0.5 (an average of 26.3) to 0.9 (an average of 26.2) percentage points when the level in the filter had not been controlled. An interesting observation is that the moisture content was not significantly affected even though the vacuum went from -60 kPa to -54 kPa. This apparently contradictory result can be explained by the fact that two mechanisms that influence the moisture content were affected at the same time. First, the weaker vacuum decreased the driving force for dewatering. Second, the residence time on the filter cloth increased as the level in the tray decreased, which enhances dewatering. The reason for the weaker vacuum is probably that a larger surface of the drum was exposed to air as the level of liquid became lower. The greater access to air increased the pressure equalization in the drum. Nevertheless, not diluting the lime-mud slurry prior to uptake on the filter appears to have had a positive effect on the dry lime-mud feed rate to the lime kiln. This, in turn, had a positive effect on the stability of the feed-end temperature since the influx of lime mud would vary less. The flow of water for level control was measured to be between 12.5 and 14.5 liter/s. The conclusion of the trial was that level control does not seem necessary and could be shut off to stabilize the dry-mud feed rate.

6 Main conclusions

The present research found that dusting at the hot end of a lime kiln is accompanied by the presence of fines in the burned lime. The fines in the study had an approximate particle size of around 50-100 μm . Several samples of reburned lime, containing both fines and granules, were taken from the discharge of the lime kiln and the chemical composition of the fines was very similar to the granules that were sampled at the same occasion. The fraction of fines in the lime had a terminal velocity of around 0.5 m/s, which means that they will be entrained with secondary air since the velocity of the secondary air through the portholes was around 5 m/s.

When slaking and causticizing fines and granules, the granules generated a faster and higher rise in temperature and a faster and greater increase in effective alkali. It was found that the lower reactivity of the fines is accompanied with a lower specific surface area.

The large fraction of fines in the reburned product and the difference in reactivity between fines and granules can likely cause variations in lime charge since the addition of lime is controlled by the increase in temperature in the slaker. The varying lime charges, therefore, can lead to periodic under- and overliming.

The periods of dusting at the hot end was accompanied by an increased power demand by the electrical drive that rotates the kiln at a given rotational speed. This increased power demand is likely explained by larger amounts of material in the kiln. A larger amount of material could possibly be explained by the presence of more fine material. The fine material has more surface and is therefore subjected to larger friction which lowers the discharge feed rate even though the lime mud feed rate remains the same.

An unexpected finding of this study was that, despite the commonly accepted relationship between sodium and adhesion between particles, variations in the sodium content in lime mud did not explain the periods of dusting in the burner zone of the kiln. Instead, findings suggest that a varying load on the ESP can influence the presence of fine material and, consequently, on the dusting at the hot end of the kiln. However, the mechanisms behind this were not completely understood. Possible explanations are that the presence of large amounts of ESP dust lead to impaired granulation or the formation of agglomerates with lower mechanical durability.

7 Future work

Three areas were identified to be of special interest for further study. These areas are:

1. *Investigate the mechanisms of nodule formation*

The findings from this study suggest that nodules might be formed at different distances from the inlet, depending on particle size and the dry feed of ESP dust. Previous investigations into residence time also suggest that there is non-linearity in the velocity of the bed of the lime kiln. This could, in part, be explained by the formation of agglomerates at different positions along the length of the kiln.

2. *Investigate an on-line method for continuously monitoring the quality of reburned lime*

Reburned lime varies notably in terms of agglomerate size, reactivity and residual CaCO_3 . However, there is no practical method for monitoring the lime after the kiln. Previous studies describe dropping a lime pellet on a steel plate and measuring the resulting sound, which correlates with the specific surface area. Other studies also use sampling robots to gather lime for an automatic analysis of the residual CaCO_3 . These methods, however, require a sampling robot, and there is great risk that the sampling procedure will influence the measurement results. The desired signal should ideally be closely tied to the reburning temperature to be useful for assessing the quality of reburned lime.

3. *Further mapping of non-process elements*

Using the vast amount of data that is available at the Mönsterås mill, thanks to extensive laboratory work and the vast instrumentation involved in the process, correlations that were previously unknown, to the knowledge of the author, were found. Extended study of the data would offer an opportunity to deepen the understanding of the chemical recovery cycle.

8 Acknowledgements

Jag vill tacka min hustru, mormor, morfar, farfar, föräldrar och Södras forskningsstiftelse. Särskilt tack till min examiner Hans Theliander, min handledare Harald Brelid och personalen på Södra Cell Mönsterås.

9 References

- Abson, D., & Holman, K.** (1985): Alternate fuels for lime kilns – effects of fuel ash on lime and liquor quality. International Chemical Recovery Conference, New Orleans, USA, 407-418.
- Andersson, S., Herstad, S., & Lindberg, H.** (1983): Mesabränning, kalkkvalitet och mesaegenskaper. STFI B 619. Stockholm
- Ankerfors, M., Fougner, K., Ivarsson, M., Hylander, N., & Norrström, H.** (2018): Teknisk potential för biodrivmedels-produktion av skogliga restprodukter och restprodukter från svensk skogsindustri. ÅF.
- Azgomi, F.** (2014): Impact of liming ratio on lime mud settling and filterability in the kraft recovery process. Thesis for doctoral degree, Department of Chemical Engineering and Applied Chemistry, University of Toronto.
- Baker, E.** (1962): The calcium oxide-carbon dioxide system in the pressure range 1-300 atmospheres. Journal of the Chemical Society, 464-470.
- Boniface, A., Mattison, R., & Haws, R.** (1968): Reausticizing systems should strike balance between your cost and their performance. Pulp and Paper, 42(44), 28-30.
- Borg, O., & Hult, N.** (1985): Vitlutsberedning. Y-24, ISBN 91-732-086-8, Sveriges skogsindustriförbund, Markaryd
- Carlhamn, E.** (1980): Synpunkter på mixeriernas utveckling. Mixerisymposium, SPCI, 2-5.
- Dernegård, H., Brelid, H., Theliander, H. & Berg, E.** (2017): Variability in lime-mud feed rate: consequences and actions. Journal of Science & Technology for Forest Products and Processes, 6(3), 19-27.
- Energimyndigheten.** (2017): Energy balance.
http://pxexternal.energimyndigheten.se/pxweb/sv/%c3%85rlig%20energibalans/%c3%85rlig%20energibalans_Balanser/EN0202_A.px/table/tableViewLayout2/?rxid=6366270f-4047-4625-880c-7a82dff6743b
- Francey, S., Tran, H., & Jones, A.** (2009): Current status of alternative fuel use in lime kilns. Tappi Journal, 8(9), 33-39.
- Hammond, W. G.** (1888): Apparatus for causticizing soda. USA Patent No. 381 996.
- Hanson, C.** (1993): Lime Mud Reburning – Properties and quality of the lime produced. Thesis for doctoral degree, Department of Chemical Engineering, Chalmers University of Technology, Göteborg.
- Hanson, C., & Theliander, H.** (1994): Properties and quality of lime Part 1. The influence of conditions during reburning. Nordic Pulp & Paper Research Journal, 9(3), 161-167.
- Holmqvist, R., & Jönsson, T.** (1993): Sintringsgrad hos mesakalk. STFI-meddelande C 265.

- International Energy Agency.** (2009): Energy technology transitions for industry. International Energy Agency.
- International Energy Agency.** (2015): Energy technology perspective. Paris, International Energy Agency.
- Izhar, M. A.** (2004): Effect of sodium compounds on particle adhesion in lime kilns. Thesis for master's degree, Department of Chemical Engineering and Applied Chemistry, University of Toronto.
- Jullander, I.** (1982): Mixeriet i brännpunkten: Teknikutvecklingen skjuter fart. Svensk Papperstidning 85(16), 32-37.
- Keitaanniemi, O., & Virkola, N.-E.** (1982): Undesirable elements in the causticizing systems. Tappi, 65(7), 89-92.
- Kuczynski, G.** (1972): Physics and chemistry of sintering. Advances in Colloid Interface Science, 3(3), 275-330.
- Lindberg, H., & Ulmgren, P.** (1986): The chemistry of the causticizing reaction – effects on the operation of the causticizing department in a kraft mill. Tappi Journal, 69(3).
- Lindblom, J., & Theliander, H.** (1998): The physical strength of lime pellets. International Chemical Recovery Conference, Tampa, USA, 561-569.
- Lindblom, J., Wildt, J., & Theliander, H.** (1998): Sintering of calcined lime mud-the influence of sodium and sulphate content in the lime. Nordic Pulp & Paper Research Journal, 3(11), 23-31.
- Manning, R., & Tran, H.** (2014): Impact of co-firing bio-fuels and fossil fuels on lime kiln operation. International Chemical Recovery Conference, Tampere, Finland, 152-162.
- Mikulcic, H., v. B., Vujanovic, M., Priesching, P., Perkovic, L., Tatschl, R., & Duic, N.** (2012): Numerical modelling of calcination reaction mechanism for cement production. Chemical Engineering Science, 69(1), 607–615.
- Niemelä, K., & Alén, R.** (1999). Characterization of pulping liquors. In E. Sjöström, & R. Raimo Alén, Analytical Methods in Wood Chemistry, Pulping, and Papermaking. Heidelberg: Springer, 193-233.
- Pietsch, W.** (2002): Agglomeration processes: Phenomena, Technologies, Equipment. Weinheim: Wiley-VCH Verlag GmbH.
- Rydin, S., Haglund, P. & Mattson, E.** (1977): Causticizing of technical green liquors with various lime qualities. Svensk Papperstidning 80(2), 54-58.
- Skogsindustrierna** (2017): Retrieved from Forest industries:
<http://miljodatabas.skogsindustrierna.org>
- Skogsindustrierna** (2018): Skogsindustrierna. Retrieved from Massa & Pappersindustrin:
<https://www.skogsindustrierna.se/skogsindustrin/branschstatistik/massa--pappersindustrin/>

Skogsstyrelsen (2017): Skogsstyrelsens statistikdatabas.

<http://pxweb.skogsstyrelsen.se/pxweb/sv/?rxid=905dbe86-d21c-4010-9e8f-992061b5aa0b>

Tegehall, L., Törmälä, J. & Jareman, F. (2017): Combined systems and detailed model of the lime kiln, ÅForsk.

Theliander, H. (1987): An analysis of a part of the recovery system of the sulfate pulp process. Thesis for doctoral degree, Department of Chemical Engineering Design, Chalmers University of Technology, Göteborg.

Theliander, H. (1988a): A system analysis of the chemical recovery plant of the kraft pulping process. Part 5. The causticizing rate, Nordic Pulp & Paper Research Journal, 3(2), 55-60.

Theliander, H. (1988b): A system analysis of the chemical recovery plant of the sulfate pulping process. Part 6. Comments on the lime reburning system. Nordic Pulp & Paper Research Journal, 3(2), 60-68.

Theliander, H. (1992): On the equilibrium of the causticizing reaction. Nordic Pulp & Paper Research Journal, 7(2), 81-87.

Thuresson, T., Johansson, A. (2016): Bioenergi från skog och skogsindustri, Pöyry Management Consulting AB.

Tran, H., Mao, X., & Barham, D. (1993): Mechanisms of ring formation in lime kilns. Journal of Pulp and Paper Science 19(4), 167-175.

Tran, H., Vollicks, S., Gauthier, M. & McNeil, C., (2007): Correlation between nodule size and residual carbonate content in lime kilns. Tappi Journal, 6(4), 9-15.

Ulmgren, P. (1997): Non-process elements in a bleached kraft pulp mill with a high degree of system closure - state of the art. Nordic Pulp & Paper Research Journal, 12(1), 32-41.

Wallbäcks, L., Theliander, H., Johanson, O., Johansson, J.-Å., & Welin, A. (2014): Stable lime kiln feed through on-line measurement and feed control. International Chemical Recovery Conference, Tampere, 170-186.

Wiesner, E. & Edfeldt, E. (2019): Klimatneutral konkurrenskraft – Kvantifiering av åtgärder i klimatfärdplaner, Sweco Energguide AB.

10 Summary of Papers I and II

10.1 Paper I

The first paper was published in Nordic Pulp & Paper Research Journal Volume 32, number 1 in 2017 and was presented at the Tappi PEERS conference in September, 2017.

Lime mud, ESP dust and reburned lime were sampled on 11 different occasions: 5 samples were taken when the kiln was heavily dusting; 5 samples were taken when the kiln was clear; and 1 sample was from a period when the kiln was only a little dusty. The reburned lime was sieved, and the different fractions were weighed. The wet lime mud, ESP dust and reburned lime were analyzed for contents of Ca, Mg, Mn, Al, Si, P, K, Zn and Fe. Carbon and sulphur contents were also determined by analyzing the CO₂ and SO₂ released during heating using an ELTRA CS 800 instrument. The enrichment of each element relative to the lime mud was calculated using the analyzed concentrations of the elements in the wet lime mud, ESP dust and reburned lime. Four samples were also taken from 2 dusting and 2 clear occasions. These samples were used to separate the fraction of fines and the fraction of granules larger than 10 mm and smaller than 15 mm. These samples were also analyzed with regard to their chemical elements and available CaO. The fines and granules were then slaked and causticized in an industry like synthetic green liquor where the increase in temperature and effective alkali was measured for 3 hours. The specific surface area of the fines and granules was also analyzed, as well as the particle size of the lime mud formed after causticizing.

Sieving and weighing of the different fractions showed that when the kiln was dusting, the fraction of fines varied from 15 to 50%. When the kiln was clear, however, the fraction of fines was only a few percent. On one clear occasion, there were no particles smaller than 1 mm. The chemical analysis of the 11 samples showed that there was no significant difference between the lime mud from a dusting or clear kiln. When the kiln was dusting, however, the sodium and potassium were significantly more enriched in the ESP dust. This result was slightly unexpected since earlier studies have shown that there is a clear onset of adhesion when the sodium level exceeds a threshold level.

The results from the slaking and causticizing of granules and fines showed that the fines systematically generated a smaller temperature increase as well as a lower increase in effective alkali compared to that of the granules. One plausible explanation is that the fines have a notably lower specific surface area (i.e. hard burned lime) and are, therefore, less reactive. Hard-burned lime generates lime mud agglomerates (size of 10-30 µm) consisting of relatively large primary particles of 0.1-1 µm (Hanson, 1993) since the particles are more sintered and require a larger force to separate the material.

An interesting observation is that the different causticizing and temperature curve profiles in Figure 14 (in Section 5.1.3) of the granules were very similar, regardless of whether the kiln was dusting or clear, hotter or colder. The curve profiles of the fines, however, differed notably more. A possible explanation might be that the fraction of granules was selected after sieving, and the reburned lime was, thus, similar in both shape and size. This would align with the findings from Tran et al. (2007) who have found a very strong relationship between the nodule diameter and the residual carbonate content of the lime pellet. All

material smaller than 1 mm was, however, categorized as fines, and it is likely that a hotter kiln, or a higher recirculation of the fine material in the burner zone of the kiln, has a negative effect on the reactivity of the lime.

The second interesting observation was that the granules and fines had almost identical chemical compositions apart from the residual carbonate. One possible explanation is that both the nodules and the fines were formed from the same lime mud or.

Paper I includes the findings from a mill trial in which all ESP dust had been removed from the loop and loaded onto a truck with a large “vacuum cleaner.” The amount was monitored with hourly readings of the axle pressure of the truck. This was done on 3 occasions: when the kiln was dusting, when it was clear and in between. It was found that the amount of recirculated ESP dust correlated positively with the amount of fines in the reburned lime produced. When the kiln was dusting, the feed rate of the ESP dust entering the kiln was high and varied more than the dry substance of lime mud from the lime mud filter (variations of +/- 0.3 ton/h compared to 0.05 ton/h). When the ESP dust was removed for 8 hours, the kiln became much clearer, going from around 25% fines to around 5% fines in the produced reburned lime.

10.2 Paper II

The second paper was published in the Journal of Science & Technology for Forest Products and Processes, volume 6, number 3 in 2017 and was presented at the International Chemical Recovery Conference in May, 2017.

The focus of the second paper is on the stability of the temperature profile of a kiln. The most important factors are the feed rate of lime mud and water entering the kiln.

Simulations showed that there is a time delay of around 1h between the time at which an action is made (e.g. increase in fuel) and a new steady state in the kiln with a different temperature profile. Therefore, a robust and reliable calculation of the reburned lime production is important to adjust fuel feed rate in proportion to the lime mud feed to the kiln.

Traditionally, production is calculated by determining the dry solids of the lime mud slurry by measuring the slurry density and correlating that to the fraction of water. The dry solids of the lime mud is then multiplied by a factor (typically 0.6) for converting 1 mol of CaCO_3 with a molar weight of 100 g/mol to CaO with a molar weight of 56 g/mol. If all CaCO_3 was converted to CaO, the factor would be 0.56. A higher factor is explained by more residual CaCO_3 and non-process elements. Measuring slurry density is troublesome since the meters have a tendency to drift, and the measurement error is multiplied by the dilution degree making the measurement troublesome.

In order to obtain a more robust and reliable production number, a Kn4-200 band scale from SEG and a NIR detector from NDC Technologies were mounted on the conveyor belt between the filter and kiln. The amount of CaCO_3 in the lime mud and the subsequent heat demand was determined by measuring the carbon content of the mud. The observation was also simulated in a dynamic model for better understanding of the mechanism and the cause of the temperature variations observed in the kiln.

A calculation procedure involving the measurement of the carbon and sulfur content in dry lime mud and burned lime was developed. The calcination degree can be estimated by measuring the residual carbonate content in the burned lime and the $\text{Ca}(\text{OH})_2$ in the lime mud. An analysis of the relative influence of the CaO in mud found that it has practically no influence within the normal range of variation and can be neglected. The available CaO was predicted using the measured carbonate content in the lime mud and the calculated calcination degree.

This procedure was evaluated by validation with lab analysis of the available CaO using the sugar method, and this showed that the calculation underestimated the available CaO when 100% of the dead load was assumed to remain in the lime mud in the burned lime. In contrast, the calculation showed good fit when only 50% of the dead load was assumed to remain in the mud in the burned lime.

The new conversion factor was validated by dumping all lime produced over a sufficient time period and weighting the lime on a calibrated scale. More recent investigations with a TGA have confirmed the new conversion factor of around 0.57.

The moisture content of the lime mud has a measurable effect on the flue gas temperature at the feed-end of the kiln by more than 1°C for every percentage point of moisture content in the lime mud, see Figure 25 in Section 5.2.1. This is not immediately obvious since lime mud is assumed to be completely dry when it enters a kiln after the flash dryer. A possible explanation could be that the dried lime mud after the flash dryer has a lower temperature when the lime mud has a high moisture content.

By using the installed equipment, periodic variations in both feed rate and moisture content were observed and correlated to the dilution of the lime mud slurry that follows from adding water to the vat to maintain a constant vat level.

Hourly variations in moisture content were observed following the movement of the water jet for precoat removal. The reason for the higher moisture content is likely that the vacuum (which is the driving force for dewatering) inside the filter is weakened when the water jet removes the precoat and exposes the filter cloth on the side of the connection to the vacuum pumps. The disturbance could probably be minimized if the water jet was positioned under instead of on the opposite side of the doctor blade since the filter cloth is exposed for a shorter time.

