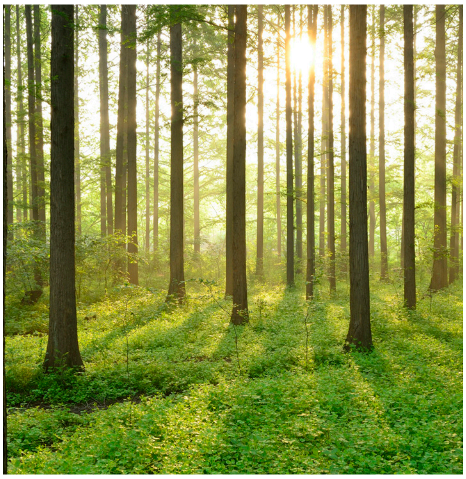
LIME KILN DUSTING

REPORT 2019:628



RESURS- OCH KLIMATEFFEKTIV
SKOGSINDUSTRI

Lime Kiln Dusting

Damning i mesaugn

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Förord

Denna rapport är slutrapportering av projekt SE214 Damning i mesaugn inom forskningsprogrammet Resurs- och Klimateffektiv skogsindustri.

Programmets handlar i första hand om energieffektivisering och att kunna nyttiggöra såväl termisk som organiskt bunden energi i pappers- och massabrukens procesströmmar. Projekt inom programmet ska ge lösningar på upplevda problem på bruken och ge möjlighet att implementera forskningsresultaten kommersiellt inom en femårsperiod.

I detta projekt har en möjlig orsak för damning i mesaugnar studerats. Det har framför allt berört upphettningshastighetens inverkan på mesapartiklarnas hållfasthet. Projektet har varit en förstudie med intentionen att visa huruvida upphettningshastigheten spelar en signifikant roll eller inte. I förlängningen kan projektet hjälpa till med underlag för få en bättre styrning på ugnen och därmed bättre kvalitet på den ombrända mesan.

Studien har genomförts av Högskolan i Borås med Tobias Richards och John Joseph som utförare. Projektets referensgrupp har varit Mikael Forssén (BillerudKorsnäs), Mats Lundberg (BillerudKorsnäs), Fredrik Lind (SCA), Henric Dernegård (Södra Cell) och Tord Hultberg (Södra Cell).

Forskningen har möjliggjorts ekonomiskt genom medel från ÅForsk samt dessa bruk:

Billerud Korsnäs Frövi
Billerud Korsnäs Gävle
Billerud Korsnäs Gruvön
Billerud Korsnäs Karlsborg
Billerud Korsnäs Skärblacka
Munksjö Aspa
SCA Munksund
SCA Obbola
SCA Östrand
Södra Cell Mönsterås
Södra Cell Mörrum
Södra Cell Värö

Samtliga bruk ovan har representanter i programstyrelsen.

Helena Sellerholm
Områdesansvarig
Termisk energiomvandling, Energiforsk AB

Sammanfattning

Damning i mesaugnar är problematiskt ur flera aspekter. Det leder till förändringar i värmeöverföringen till mesapartiklarna och hur mycket hårdbränt material som produceras i ugnen. Förändringarna kan leda till minskad kvalitet på den ombrända mesan och en minskad produktionskapacitet. I detta projekt har en av flera olika möjliga orsaker till damningens uppkomst studerats, nämligen att upphettningshastigheten hos de inkommande mesapartiklarna kan påverka dess hållfasthet. En svagare partikel kan enklare brytas sönder och därmed bilda finpartikulärt damm.

Projektet har varit en förstudie med ett begränsat antal försök och samtidigt fyra olika material att studera. Det var inte möjligt under detta projekt att helt separera olika effekter som påverkar en eventuell damning. De olika mekanismerna som sker simultant är dels kemisk reaktion (primärt kalcineringsreaktionen) och dels nodulbildning och agglomerering som beror på partiklarna initiala egenskaper som ytråhet men även på den kemiska sammansättningen. Utöver detta så är mass- och värmetransport väsentliga inslag och påverkas av partiklarnas rörelser och mekanismen för värmeöverföring samt gashastigheten. Det har varit en tendens i försöken med tvättad mesa att ökad upphettningshastighet kan ge en större andel finare partiklar (mindre än 125 μm) vilket i sin tur avspeglar sig en högre kalcineringsgrad. Mesa i form av elfilterstoft beter sig annorlunda än den vanliga mesan vilket beror på den kemiska sammansättningen och speciellt den höga halten av natrium. Denna mesa bildade betydligt fler stora partiklar som dessutom var relativt starka men visade också tendensen att högre upphettningshastighet gav mindre partiklar.

Andra testade parametrar var varierad grad av koldioxid (0 eller 20 %) och rotationshastigheten (1 eller 2 rpm). Koldioxiden påverkade kalcineringsgraden negativt men hade en liten inverkan på partikelstorleksfördelningen. En tendens var att det fanns fler mindre partiklar för mesan från elfiltret efter tillsats av koldioxid. Rotationshastighetens påverkan på storleksfördelningen var svag.

Summary

Dusting in lime kilns is problematic from many perspectives. It will change the heat transfer to the lime particles and thereby the amount of hard burnt material produced in the kiln. This will cause reduced quality of the reburned lime mud and a loss in production capacity of white liquor. In this project, one of several possible causes for lime kiln dusting has been investigated. Namely that the heat rate of the incoming lime mud particles may affect their stability and strength. A weaker particle can more easily brake down and form fine dust.

This project has been a pre study with a limited number of experiments and at the same time four different materials to study. It was not possible to distinguish between the different effects that may cause dusting. Several different mechanisms occur simultaneously and these are mainly: chemical reaction (primarily the calcination reaction) and nodule formation and agglomeration which depends on the properties of the material like surface roughness and chemical composition. In addition, mass and heat transfer are important parts and depends on the movements of the particles and the heat transfer mechanism and surrounding gas flow pattern and velocity. There has been a tendency in the experiments with ordinary washed lime mud that an increased heating rate give a larger fraction of fine particles (particles less than 125 μm) which reflects in a higher degree of calcination. Lime from the electrostatic precipitator behaves rather different than the ordinary lime mud which depends on the chemical composition and especially the high amount of sodium. This lime formed much larger and stronger particles. This lime also had a shifted particle size distribution towards smaller sizes at higher heating rates.

Other tested parameters was the amount of carbon dioxide (0 or 20 %) and rotational speed (1 or 2 rpm). Carbon dioxide affected the degree of calcination negatively but had only a small impact on the particle size distribution. A tendency was that there was more small particles for the lime from the electrostatic precipitator with higher amount of carbon dioxide. The rotational speed had a weak interaction with particle size distribution.

Utökad sammanfattning Damning i mesaugn

Syfte och mål

Syftet med detta projekt är att studera upphettningshastighetens påverkan på mesapartiklarnas hållfasthet i mesaugnen. Detta är viktigt för att kunna förstå orsakerna bakom damning i ugnen och som kan leda till försämrade driftsbetingelser och ökat behov av underhåll. Målet är att bestämma partikelstyrkan hos fyra olika industriella mesor när de genomgår en kontrollerad upphettning i en elektriskt upphettad roterugn.

Introduktion

En viktig del vid kemikalieåtervinningen i sulfatmassabruk är produktionen av bränd kalk (CaO). Den brända kalken används för att generera natrium hydroxid (NaOH) som behövs för att separera vedens beståndsdelar i kokaren. Vid produktionen av NaOH bildas även mesa ($CaCO_3$) och denna förening kan omvandlas till CaO i mesaugnen och skapar därigenom en materialloop och minskar behovet av ny råvara. Mesaugnen är en roterugn som kan vara över 100 m lång och flera meter i diameter. Den har en svag lutning fån inloppet till utloppet och rotationen hjälper till att förflytta materialet i lagom takt för att reaktionen ska hinna klart. Utöver den kemiska reaktionen är också den fysiska förändringen av partiklarna genom graden av agglomerering och sintring viktig. Stora partiklar tar lång tid för efterföljande reaktioner och kan även vara svåra att få tillräcklig omsättningsgrad i ugnen. Små partiklar kan å andra sidan leda till separationsproblem när mesan ska avskiljas.

I mesaugen är syftet att mesa ska reagera till bränd kalk, som även benämns ombränd mesa. Det görs genom reaktionen:

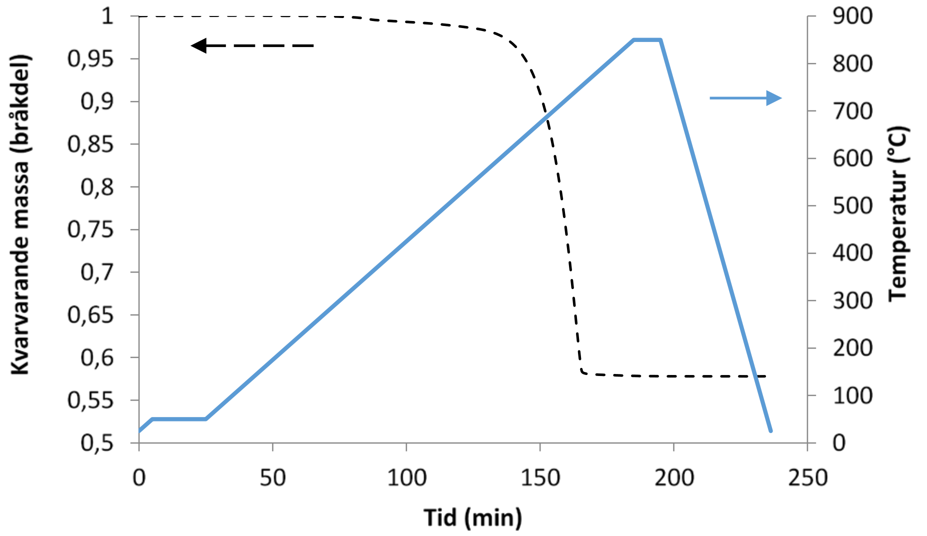
$CaCO_3 \rightarrow CaO + CO_2$

Reaktionen förutsätter en hög temperatur vilket innebär att energi måste tillföras till ugnen. Det görs genom att förbränna ett bränsle vid utloppet och där sedan rökgaserna går i motsatt riktning jämfört med det fasta materialet. Sluttemperaturen över 1000°C vilket ger möjligheter för att partiklarna ska sintra och bilda starkare enheter och minska risken för finpartikulärt material. Ett problem som kan uppstå i mesaugnen är att det bildas små partiklar som dras med i gasflödet som ett damm. Detta förändrar temperaturprofilen i ugnen eftersom en del strålningsvärme tas upp av dammet och därmed flyttas energi till andra delar i ugnen. Flera olika problem kan orsakas av detta fenomen och de viktigaste är ökad mängd fast material i ugnen, ökad risk för ringbildning, ökad bränsleförbrukning samt ökat behov av underhåll. Att damningen startar har olika orsaker. Det kan vara beroende på den kemiska sammansättningen hos den inkommande mesan och den ombrända kalken eller den fysiska miljön i ugnen såsom temperatur, halt av CO_2 och uppehållstid.

I detta projekt studeras upphettningshastighetens inverkan på dammbildningen. Hypotesen är att en långsam upphettningshastighet ger möjlighet för att reaktionen ska hinna klart innan sintringen av partiklarna startar. Detta är viktigt eftersom reaktion till bränd kalk ändrar volymen och därmed kan påverka hållfastheten för partiklarnas inre delar vilket kan leda till att de lättare bryts sönder.

Metod

Fyra olika material har används för studien. Det är tvättad mesa från SCA Munksund (prov L1), Södra Cell Värö (prov L2), KorsnäsBillerud Skärblacka (prov L3) samt material från ESP filter efter mesatorken från ett av Södra Cells bruk (prov L4). Alla dessa material går vanligtvis in i mesaugnen. Den kemiska sammansättningen på de tre tvättade mesorna var relativt lika med skillnader framför allt i halt Ca (50-56% räknat som CaO), Si (0.18-0.54% räknat som SiO_2) samt P (1.16-1.48% räknat som P_2O_5). Prov L4 hade en mer än dubbelt så hög halt av Na och P jämfört med övriga prov. Storleksmässigt hade prov L1 och L3 ungefär storleksfördelning med en medelstorlek omkring 36 μm, prov L2 hade en medelstorlek på 24 μm medan prov L4 endast hade en medelstorlek på 6 μm. Reaktiviteten och därmed tillgänglig $CaCO_3$ hos de olika materialen testades med en termogravimetrisk våg som väger provet samtidigt som temperaturen kan kontrolleras (figur S1 visar ett exempel med prov L1). Prov L4 hade minst mängd $CaCO_3$ och fick en viktminskning med 40% medan de övriga materialen minskade vikten med över 41% (41.7-42.6 %).

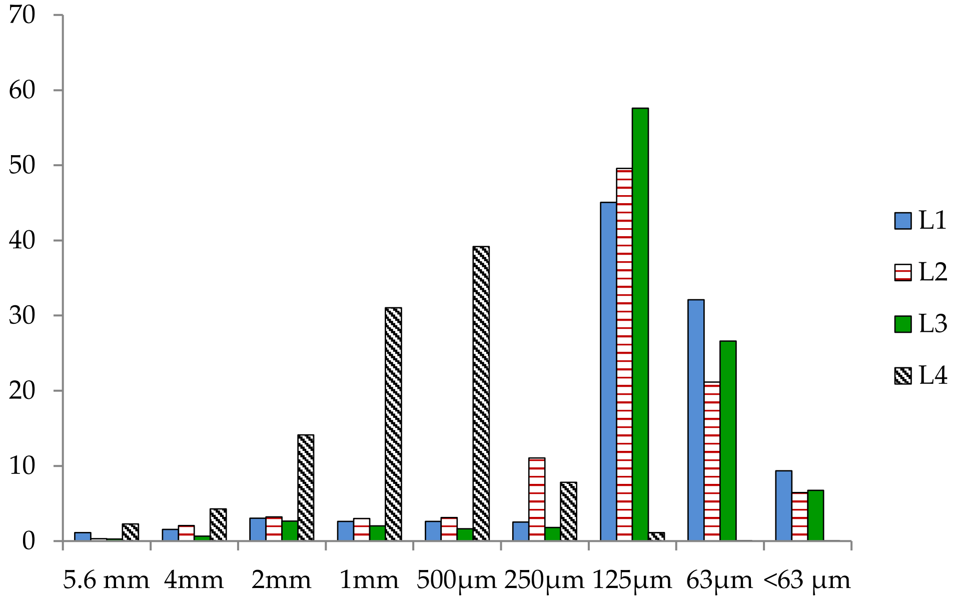


Figur S1. Viktminskning under kalcinering av prov L1 upp till 850°C

Den huvudsakliga utrustningen för försöken har varit en laboratorieskala modell av en roterugn med en längd av 1125 mm och en innerdiameter av 190 mm. Ugnen är elektriskt upphettad vilket gör det möjligt att styra upphettningshastigheten (5 till 20 °C/min). Dessutom går det att variera rotationshastigheten (1 - 2 rpm) och sammansättningen på omgivande gas genom inblandning av CO_2 (0, 20 eller 100%). De flesta försök genomfördes med en maximal temperatur på 850°C men även 950°C användes. Både dessa temperaturer är lägre än vad som återfinns i slutskedet av mesaugnen men eftersom syftet är att studera partikelhållfastheten vid agglomereringen så antas resultaten vara extrapolerbara för att påvisa effekten även vid högre sluttemperaturer och därmed vid en ökad sintring. Uppehållstiden var 1 timme vid den maximala temperaturen och därefter fick ugnen svalna under 12 timmar innan provet togs ut. Totalt genomfördes 38 experiment. Efter genomförda försök analyserades materialet med avseende på halt av restkarbonat, B.E.T. ytarea samt styrka. Ytarean är relaterad till styrkeegenskaper och indikerar graden av sintring. Styrkan testades genom siktning i två steg. Först ett steg med mild skakning under siktningen vilket då gav en storleksfördelning som motsvara den i ugnen under antagandet att partiklarna inte slås sönder. Steg två innebär en betydligt kraftigare skakning och också under längre tid. En jämförelse av storleksfördelningen mellan de två stegen indikerar hållfastheten för materialet.

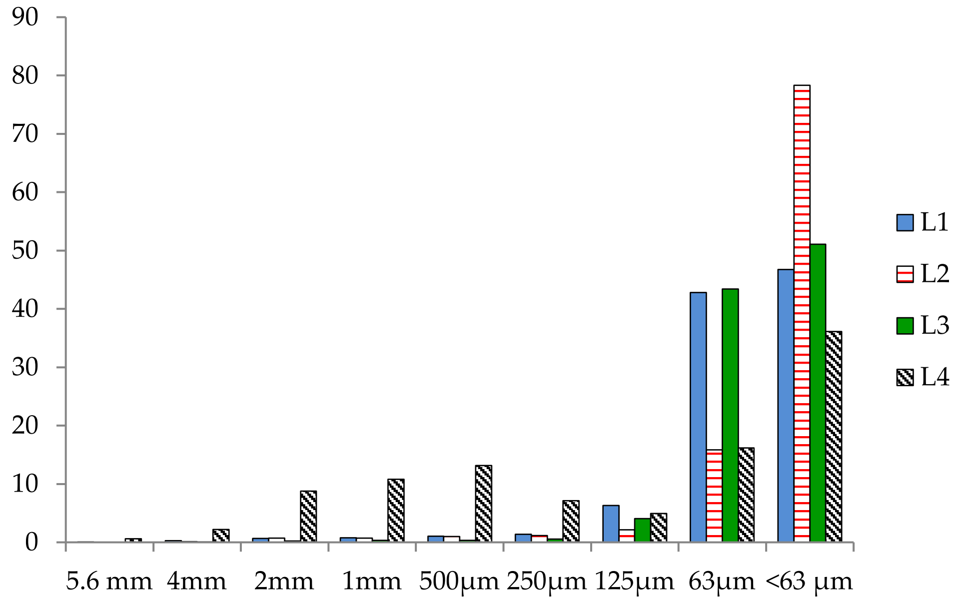
Resultat och diskussion

Det var tydligt att partiklarna som bildas efter agglomereringen i ugnen är relativt spröda och har låg hållfasthet. De tvättade mesorna (prov L1-L3) hade främst partiklar mellan 120 och 250 µm medan ESP provet agglomererade betydligt mer och trots mindre partiklar från start så erhölls störst andel av partiklar mellan 500 µm och 2 mm, figur S2.



Figur S2. Partikelstorleksfördelning för de olika ursprungsproverna efter mild siktning vid en upphettningshastighet av 10 °C/min och en maximal temperatur på 850°C

Efter den kraftigare skakningen så förändrades storleksfördelningen och den största andelen var mindre än 125 µm och endast prov L4 hade signifikanta mängder av partiklar som var större än 250 µm, figur S3. Att prov L4 hade större partiklar beror på skillnaden i kemisk sammansättning där framför allt mängden natrium är betydligt högre. Detta var återkommande för de alla försök (tabell S1 och S2). Tydligt är att partiklarna vid den högre temperaturen blir större. Eftersom halten av restkarbonat i prov 4 var högre jämfört med övriga prov så verkar agglomereringen av mindre partiklar till noduler ske tidigare för detta prov och delvis överlappa kalcineringsreaktionen. Detta innebär att den totala reaktionshastigheten minskar.



Figur S3. Partikelstorleksfördelning för de olika ursprungsproverna efter kraftig siktning vid en upphettningshastighet av 10 °C/min och en maximal temperatur på 850°C

Tabell S1: Andel ombränd mesa större än 250µm efter mild siktning.

Ramp	**Gas**	**L1 (vikt %)**		**L2 (vikt %)**		**L3 (vikt %)**		**L4 (vikt %)**	
(°C/min)		850°C	950°C	850°C	950°C	850°C		850°C	950°C
5	N_2	22	31	34	38	17	29	87	95
10	N_2	15±1	19	23	29	13±4	21	77±1	95
10	N_2,CO_2	16	N. A	32	N. A	15	N. A	94	N. A.
20	N_2	15	16	16	17	14	18	80	95

Tabell S2: Andel ombränd mesa större än 250µm efter kraftig siktning.

Ramp	**Gas**	**L1 (vikt %)**		**L2 (vikt %)**		**L3 (vikt %)**		**L4 (vikt %)**	
(°C/min)		850°C	950°C	850°C	950°C	850°C	950°C	850°C	950°C
5	N_2	4	4	2	7	1	1	33	35
10	N_2	4±0	7	3±0	10	1±0	4	40±8	57
10	N_2,CO_2	4	N. A	9	N. A	2	N. A	65	N. A.
20	N_2	7	4	7	5	2	4	53	65

Ytterligare indikation på hållfastheten är genom analyser av ytarean där en minskad ytarea reflekterar en ökad sintring och därmed en starkare partikel. Emellertid kunde inte något samband mellan minskad ytarea och större hållfasthet beläggas Det framkom att ökad upphettningshastighet tenderade ge mindre ytarea men detta gav inte utslag i hur stor andel av partiklarna som gick sönder vid den kraftigare siktningen.

En förändring av halten CO_2 i ugnen ökade mängden restkarbonat men partikelstorleksfördelningen var i princip opåverkad för båda stegen i siktningen vilket indikerar på att denna parameter inte har så stor betydelse för hållfastheten. Att ändra rotationshastigheten, vilket innebär en större fysisk påverkan i ugnen, verkade inte heller få ett stort utslag.

Mängden restkarbonat tenderade att minska med ökad upphettningshastighet. En ökad upphettningshastighet innebär att den totala tiden för försöket minskade och framför allt att tiden från starten för kalcineringsreaktionen minskade (om starttemperaturen i ren kvävgas antas till 700°C så varierar totaltiden innan försöksavslut mellan 65 och 80 min). Detta indikerar att det skett en agglomerering innan kalcineringen är avslutad och att denna blir tydligare med låg upphettningshastighet vilket därmed sänker reaktionshastigheten.

Slutsatser

Det var tydligt att provet med ESP material (prov L4) beter sig annorlunda än övriga prover med tvättad mesa. De största skillnaderna på ingående material är att prov L4 har en betydligt mindre storleksfördelning och att den kemiska sammansättningen varierar där framför allt halten av natrium är utmärkande. Detta leder till mer utmärkande agglomeration och att en minskad reaktionsomsättning. Av de övriga proven visar prov L2 den största mängden av små partiklar (mindre än 63 µm) efter kraftig siktning och indikerar därvid den största risken för damning. Det som urskilde detta prov från övriga tvättade mesaprov var att halten av Ca var lägst (och även mängd reaktiv $CaCO_3$) och att den initiala partikelstorleksfördelningen var minst.

Det fanns en tendens att en högre upphettningshastighet gav en mindre storleksfördelning vilket då i sin tur kan öka mängden damning i mesaugnen eftersom energi kan transporteras längre i ugnen genom dammpartiklarna och därigenom öka upphettningshastigheten.

Andra testade parametrar var varierad grad av koldioxid (0 eller 20 %) och rotationshastigheten (1 eller 2 rpm). Koldioxiden påverkade kalcineringsgraden negativt men hade en liten inverkan på partikelstorleksfördelningen. En tendens var att det fanns fler mindre partiklar för mesan från elfiltret efter tillsats av koldioxid. Rotationshastighetens påverkan på storleksfördelningen var svag.

Content

1 Introduction

The Kraft process is the most popular pulping process in the paper and the pulp industry (Nohlgren and Sinquefield, 2004). One advantage of this process is the recovery of chemicals used. Sodium hydroxide (NaOH) and sodium sulfide (Na_2S) which are used in the digestion and the delignification of the wood chips are recovered through various operations. The regeneration of Na_2S takes places in the recovery boiler where sulfate ions (SO_4^{2-}) and other oxidized forms of sulfur (S), such as tetrathionate ($S_4O_6^{2-}$) and thiosulfate ($S_2O_3^{2-}$), are reduced to sulfide. In addition to the recovery of sulfide, the recovery boiler also provides heat and power from the combustion of the organics present in the spent cooking liquor originating from the pulping process. The solid output from the recovery boiler is termed green liquor after it is mixed with water (weak white wash from washing the lime mud cake) and it mainly contains sodium carbonate (Na_2CO_3) and Na_2S dissolved in the water. Also some oxidized sulfur compounds are present due to incomplete reduction reactions in the recovery boiler. NaOH is produced in the causticizers where slaked lime ($Ca(OH)_2$) reacts with the Na_2CO_3 in the green liquor. At the same time, also calcium carbonate ($CaCO_3$) is formed, *(Reaction 1*). A lime kiln converts the lime mud ($CaCO_3$) into reburned lime (CaO) which produces slaked lime when added to a water solution (*Reaction 2, 3*).

$$Ca(OH)_2 + Na_2CO_3(aq) \leftrightarrow 2NaOH(aq) + CaCO_3 \quad \Delta H_{373K} = -4.2\ kJ/mol \qquad (1)$$

$$CaCO_3 \ \rightarrow CaO(s) + CO_2(g) \qquad \Delta H_{1173K} = 166.1\ kJ\ \ /mol \qquad (2)$$

$$CaO +\ H_2O\ \rightarrow Ca(OH)_2 \qquad \Delta H_{373K} =\ -67.2\ kJ/mol \qquad (3)$$

The quality of the lime determines the conversion and the efficiency of the slaking and the causticizing reactions. In addition to a good reactivity, the lime mud should be easily separable from the white liquor after the causticizers (Lindblom, 1999). The size of the lime agglomerates from the lime kiln indicates the quality of lime. The size of the lime particles is controlled by the conditions in the lime kiln.

Lindblom (1999) summarizes the relationship between lime kiln conditions and the lime particle properties and elaborates on how it impacts the quality of lime. In brief, lime that has only slightly sintered in the lime kiln forms smaller agglomerates that are more reactive but are more difficult to separate from the white liquor. Larger agglomerates, on the other hand, have sintered better but are less reactive (lower reaction rate). Lindblom, Hanson and Theliander (1996) studied the influence of carbon dioxide (CO_2) on the sintering rate of calcined lime mud. They found that the presence of carbon dioxide increased the rate of sintering but on the other hand it decreases the conversion of lime mud in the kiln.

The physical characteristics of the lime particles are responsible for the behavior in the lime kiln. Lime particles with low strength forms dust in the lime kiln and create problems in the operation of the lime kiln. Termed dusting, it can result in kiln shutdowns and unstable kiln operations (Tran 2007).

It is therefore important to study the effect of kiln characteristics on the lime particle properties. Lindblom, Hanson and Theliander (1996) and Lindblom, Wildt and Theliander (1998) investigated the influence of temperature, residence time, the partial pressure of CO_2 and, finally, the composition of the lime mud on the sintering of calcined lime mud.

The current study is intended as a pre-study and investigates the effect of the heating rate, the final temperature and the atmosphere on the degree of dusting of reburned lime particles in a pilot scale rotary kiln. Four different lime samples from Swedish mills were used. One sample was lime dust from the ESP after the lime kiln. This will contain smaller particles and also more contaminations. The potential of the lime particles to form dust is determined by the strength of the particle and this in its turn depends on the degree of sintering. Particles that retain their structure while being subjected to mechanical forces are less prone to form dust in the lime kiln. Similarly, sintering causes the particles to form nodules preventing dusting. The current investigation limits the study to the calcination zone of the lime kiln.

The hypothesis is that nodule formation and mechanical strengths are benefitted by a slow heating rate, as the reaction will be more complete before sintering. We have not proceeded to the high temperatures present in the real lime kilns which mean that the actual numbers are not directly transferrable to real conditions, but the trend should be similar as a weaker particle will only partly be compensated by a more sintered surface. From this it would suggest that a high heating rate would provide less stable particles and thus increase the dusting.

1.1 THE LIME KILN

Lime kilns are rotary furnaces made up of steel tubes. These kilns are rather large and could be several meters in diameter and more than 100 m long. The steel tubes are inclined along the horizontal axis and lined with refractory bricks on the inside. The thickness of the refractory lining ranges from 15 cm to 25 cm and the kiln rotates at around 0.5 to 2 rpm.

Lime mud ($CaCO_3$) is feed uphill and due to the inclination and the rotation of the kiln, makes its way down the kiln to the discharge end towards the burner. The burner provides heat for the drying and the calcining of the lime mud into reburned lime (Tran 2007).

Due to the length of the lime kiln and the heat source at one end, there are different temperatures inside the lime kiln. The end of the kiln where the lime mud is fed is known as the cold end due to the low gas temperature in this region while the opposite end is known as the hot end.

The drying of the lime mud begins at the cold end (or often before when a lime mud dryer and preheater are installed to better utilize the flue gases and increase the capacity of the lime kiln). As the lime mud moves further into the kiln, the temperature in the kiln begins to rise. The lime mud begins to calcine when it reaches a temperature of about 800°C (note that the concentration of CO_2 inside a lime kiln could reach 20% depending on fuel and that it locally could be even higher). During calcination, $CaCO_3$ decomposes to CaO and CO_2. This is consistent with the equilibrium CO_2 partial pressure for the calcination reaction according to Figure 1. The temperature of the lime mud remains rather constant as the calcination reaction is a strongly endothermic reaction. The calcined particles are then sintered at the higher temperatures found in the hot end of the lime kiln.

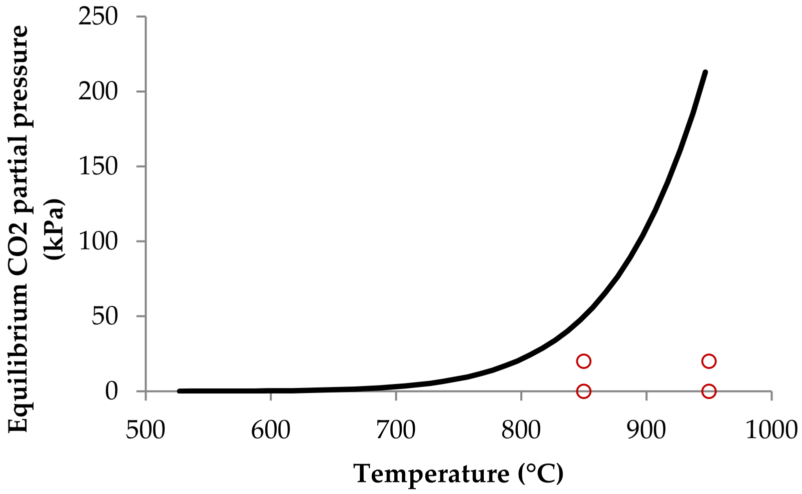


Figure 1. Equilibrium partial pressure of CO_2 during calcination (data from Valverde et al. 2015). The red circular markers shows the experimental conditions used in this study.

1.2 THE REBURNED LIME

The reburned lime obtained from the lime kiln must be of good quality. Good quality reburned lime has a low residual $CaCO_3$ content (1.5-2.5 wt. %), a high CaO content which is termed as availability (85-95%) and a porous structure to ensure a quick slaking reaction (a few minutes). The size of the reburned lime indicates the quality; it can either be powdery or in the form of nodules with an average diameter ranging from 5-50 mm. Nodules that are smaller leads to particle entrainment, dust recirculation and filtration problems while larger nodules may have more residual carbonate due to incomplete calcination. Sintering causes the lime particles to agglomerate; a high degree of sintering leads to larger particles that have a low specific surface area and that have not been calcined uniformly while low degree of sintering leads to dusting. However, the size may not always be a good indicator for the quality of the reburned lime. In the study by Dernegård, Brelid and Theliander (2017), it was found that the smaller reburned lime particles had sintered the most and was less reactive during both the slaking and the causticizing reactions compared to the larger granules.

1.3 DUSTING

The movement of the lime mud in the kiln causes dust to be formed. This dust is collected by the precipitators and scrubbers and ultimately returns to the feed end side of the kiln. Excessive dusting increases the load on these dust collection and handling systems. Apart from this, dusting also hinders the kiln production as the production must be stopped for maintenance of the dust collection systems and dusting also lowers the thermal efficiency of the kiln (Websdale, Downing and Tran 2007). The particle size is the most important parameter that determines the extent of dusting. The particle size is controlled by the degree of agglomeration of lime mud fed into the kiln and of the lime particles within the calcination zone of the kiln (Tran 2007). The presence of compounds such as sodium compounds in the lime that lowers the melting point affects the agglomeration of the lime particles in the calcination zone of the lime kiln.

Lindblom and Theliander (1999) investigated the effect of temperature, compact pressure, sintering time on the strength of the calcined lime particles. The lime mud was calcined and sintered in a laboratory furnace at temperatures between 900°C and 1200°C. It was found that longer sintering times and higher temperatures of sintering decreased the specific surface area of particles while increasing the strength of the particles.

2 Experimental

2.1 MATERIALS AND EQUIPMENT

2.1.1 Lime mud samples

Lime mud samples were obtained from four paper pulp mills in Sweden. Initially the $CaCO_3$ content of the lime samples were determined with the help of a thermogravimetric analyser. The samples were heated to 850 °C at heating rates between 5 K/min and 20 K/min in a nitrogen atmosphere using a Mettler Toledo thermogravimetric analyzer (TGA/DSC 3+). Each condition was performed in triplicates and there was a high consistency between the samples (see Figure 2 for example with sample L1) except for sample L3 where there was a deviance of about 7% between highest and lowest. As can be seen, the mass loss starts already at about 600 °C and is completed at 750 °C (this is for a fine grinded material with no CO_2 present). Analysis by ALS Scandinavia for LOI (loss of ignition) at 1000°C confirmed the measured values. The mass losses are summarized in Table 1.

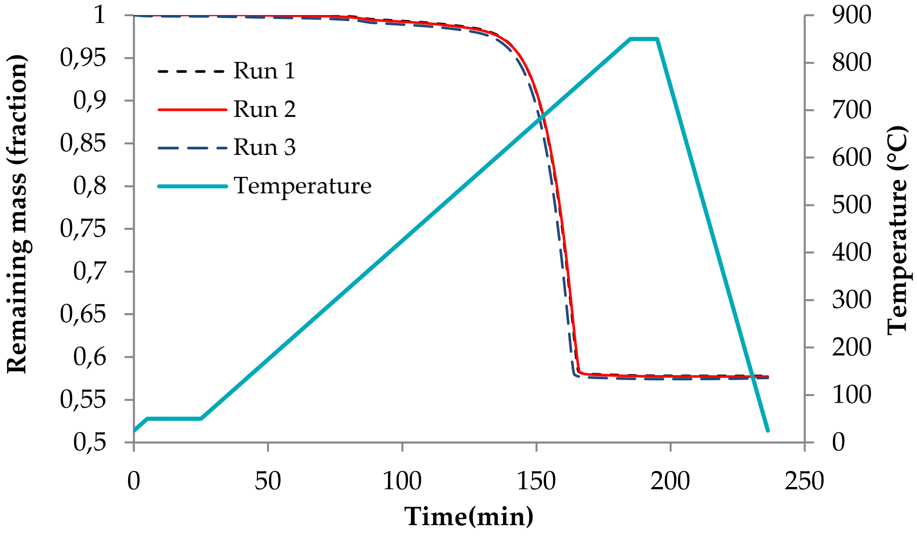


Figure 2. Mass loss during calcination of lime mud sample L1 at 850°C

The samples were sent to ALS Scandinavia AB for the more detailed chemical analysis. Table 2 displays the chemical composition of the lime samples. The chemical composition of the ESP lime sample was analyzed by Södra Cell at Mönsterås (Table 3). The particle size distribution of the lime mud samples was analyzed using a laser diffraction analysis (Table 4) at Chalmers University of Technology.

Table 1: Mass loss during LOI tests at 1000°C and own measurements at 850°C of the lime mud samples

Lime mud sample	% mass loss (1000°C)	% mass loss (850°C)
L1 SCA (Munksund)	42.6	42.6
L2 Södra Cell (Varö)	41.7	41.7
L3 KorsnäsBillerud (Skärblacka)	42.2	41.9
L4 Södra Cell ESP	Not tested	40.0

Table 2: The chemical composition of the lime mud samples

ELEMENT	SAMPLE	L1	L2	L3
TS	%	99.90	99.90	99.90
SiO_2	% TS	0.21	0.18	0.54
Al_2O_3	% TS	0.05	0.08	0.06
CaO	% TS	55.80	50.60	52.60
Fe_2O_3	% TS	0.04	0.04	0.05
K_2O	% TS	0.03	0.03	<0.02
MgO	% TS	0.67	1.13	0.90
MnO	% TS	0.04	0.08	0.09
Na_2O	% TS	0.94	1.06	1.05
P_2O_5	% TS	1.16	1.48	1.46
TiO_2	% TS	0.01	0.01	0.01
Sum	% TS	58.90	54.70	56.80

Table 3: Chemical composition of sample L4

Metal	mg/g	Element	% TS
Na	15.8	Na_2O	2.13
Mg	7.2	MgO	1.19
Mn	0.44	MnO	0.06
Al	0.60	Al_2O_3	0.11
Fe	0.20	Fe_2O_3	0.10
Zn	0.60		
P	17	P_2O_5	3.89
S	10.8		
Ca	400	CaO	55.96
Cu	<0.01		

Table 4: Particle size distribution of the lime mud samples

Sample	d(0.1)µm	d(0.5)µm	d(0.9)µm
L1	13.53	34.44	67.46
L2	9.44	24.79	49.25
L3	14.38	38.27	75.95
L4	1.77	6.48	15.07

2.1.2 Rotary lime kiln

The calcination and sintering of the lime mud were performed in a pilot scale rotary kiln. It is made of high-temperature steel (253 MA) and has a length of 1125 mm and an internal diameter of 190 mm. The kiln is powered by 3 electrical heating elements along the length of the kiln. The heating rate and the temperature of the heating elements can be controlled independently by PID controllers (Eurotherm 2116) and the maximum operation temperature is 1000°C. The rotary kiln can rotate at a maximum speed of 6 rpm, however for the current experiments the speed was set to 1 rpm. The atmosphere in the kiln can be controlled by adjusting the composition of air, nitrogen and carbon dioxide. Further details can be found in Lindblom and Theliander (2001).

2.1.3 Sieves

A Haver EML 200 Pure test sieve shaker with standard wire mesh sieves (Impact) of aperture size 5.6 mm, 4 mm, 2 mm, 1 mm, 500 µm, 250 µm, 125 µm and 63 µm was used to achieve an indication of the degree of agglomeration and the strength of the reburned lime particles.

2.2 PROCEDURE

2.2.1 The rotary lime kiln

The lime mud samples were dried for 24 hours in a muffle furnace at 105 °C before being fed into the pilot scale rotary kiln for the calcination. One end of the kiln was opened up and about 300 g of dried lime mud was loaded into the center of the kiln. A few tests were also performed with the double amount of material. After loading the lime mud into the kiln, the gas flow was turned on and the kiln was heated to the desired calcination temperature (either 850 °C or 950 °C) at heating rates of 5 K/min, 10 K/min or 20 K/min. The volume of the gas stream was maintained at 3 l/min throughout the heating and the calcination. After attaining the desired temperature, the samples were allowed to calcine and sinter in the kiln for 1 hour after which the heat supply was turned off and the kiln was left to cool overnight Figure 3.

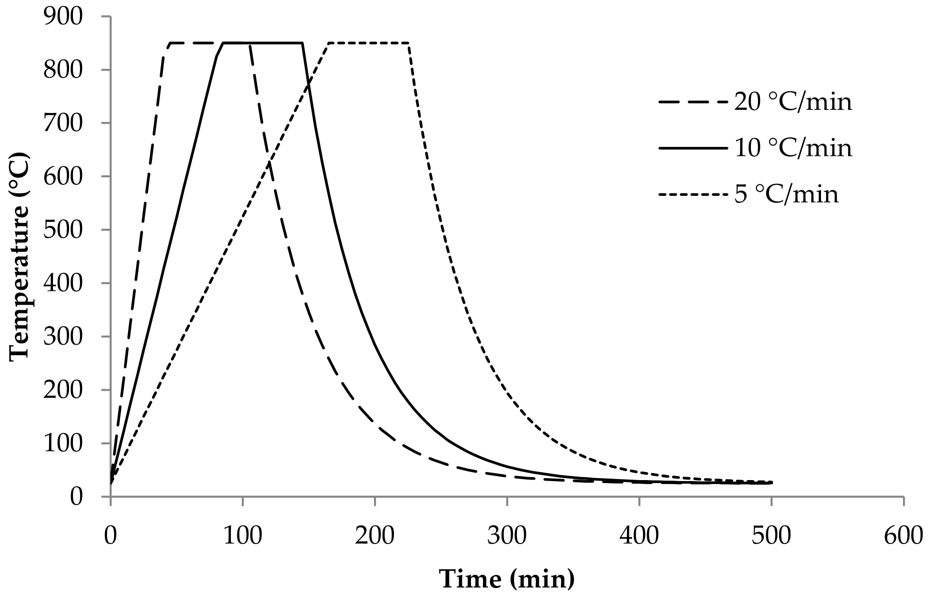


Figure 3. Temperature profile during the rotary kiln tests

In order to prevent recarbonization, a steady stream of nitrogen at 3 l/min was supplied. In order to investigate the effect of CO_2 on the lime dusting, the experiments were performed with two different atmospheres; one with a 100% N_2 gas stream and the other a mixture of nitrogen and carbon dioxide in the molar ratio 4:1 (corresponds to a CO_2 partial pressure of 20.3 kPa).

The procedure was repeated for the different lime mud samples with replicates performed for the case at 850 °C and pure N_2. Once the kiln had cooled down, the ends of the kiln were opened and the calcined lime was collected and sieved. Upon sieving, the particles of the various size fractions were mixed and the extent of calcination of the sample was analyzed by measuring the weight loss in a thermogravimetric analyzer (which is related to the amount of $CaCO_3$).

2.2.2 Sieving

Following calcination, the sample was sieved gently for 30 seconds (noted as fine sieving) and the size fractions were determined. After this, a more severe sieving took place (noted as coarse sieving). During the coarse sieving the particles were shaken more forcefully for 2 minutes. The weight fractions of the sample retained in the sieves were noted after the sieving. A part of the particles that were retained on the 1 mm and 2 mm sieves were collected. The specific surface area of these particles was then measured by BET analysis, which was performed at Chalmers University of Technology (Nuclear chemistry and Industrial materials recycling) using a Micromeretics ASAS 2020. The fine sieving can be said to represent the actual particle size distribution within the equipment and the coarse sieving indicates the strengths of the agglomerates.

2.2.3 Experimental plan

This was a limited investigation and only a limited number of experiments were scheduled. Initially, 25 experiments were suggested. This included three different lime mud samples at two temperatures (850 and 950°C) and three heating rates (5, 10 and 20 °C/min). Besides, a couple of experiments with presence of CO_2 were planned. It was however, possible to increase the number of lime mud sample and thereby also include a sample with enriched amount of other inorganics and with a smaller particle size (captured lime mud after the lime mud dryer, sample L4). In total, 38 experimental runs were performed, Table 5.

Table 5. Experiments in the rotary lime kiln

Sample No	sample	Heating rate (°C/min)	Temperature (°C)	gas	Mass (g)
1	L1	5	850	N_2	300
2	L2	10	850	N_2	300
3	L1	20	850	N_2	300
4	L4	5	850	N_2	300
5	L2	20	850	N_2	300
6	L4	10	850	N_2	300
7	L1	10	850	N_2	300
8	L4	20	850	N_2	300
9	L2	5	850	N_2	300
10	L1	10	850	N_2,CO_2	300
11	L4	10	850	N_2, CO_2	300
12	L2	20	850	N_2, CO_2	600
13	L4	10	850	N_2, CO_2	600
14	L1	10	850	N_2, CO_2	600
15	L1	10	850	N_2	600
16	L1, (2rpm)	10	850	N_2	600
17	L2	10	850	N_2, CO_2	600
18	L2	10	850	N_2	300
19	L4	10	850	N_2	300
20	L3	10	850	N_2	300
21	L3	20	850	N_2	300
22	L3	5	850	N_2	300
23	L3	10	850	N_2, CO_2	300
24	L3	10	850	N_2	300
25	L2	5	950	N_2	300
26	L1	10	950	N_2	300
27	L3	20	950	N_2	300
28	L4	5	950	N_2	300
29	L4	10	950	N_2	300
30	L2	20	950	N_2	300
31	L1	5	950	N_2	300

Sample No	sample	Heating rate (°C/min)	Temperature (°C)	gas	Mass (g)
32	L4	20	950	N_2	300
33	L3	10	950	N_2	300
34	L3	5	950	N_2	300
35	L1	20	950	N_2	300
36	L2	10	950	N_2	300
37	L1	10	850	N_2	300
38	L4	10	850	N_2, CO_2	300

3 Results

The results from the sieving as well as the combined results of the sieving and the TGA analysis of the reburned lime particles are compiled in the form of a table for the different lime samples. They are listed in Appendix A.

3.1 ANALYSIS OF THE LIME MUD

The lime samples were found to have different chemical composition and particle size distribution. The ESP dust (sample L4) contains the highest amount of sodium while the lime mud in sample L1 contains the least.

These above differences explain the observations of the thermogravimetric analysis (Table 1) where samples L1 and L3 contains higher amount of calcium carbonate and also showed the highest mass loss.

The samples had different particle sizes and especially the sample L4 had a small average size (Table 4). However, it was quite large difference between the other samples as well where sample L2 was significantly lower than samples L1 and L3. Due to the differences mentioned above, it is expected that the lime mud samples would behave differently in the pilot scale rotary lime kiln.

3.2 SIEVING

In general, the amount of small particles (particles less than 63 μm) found in after the fine sieving is less than 10% of the total amount. However, this change dramatically upon a coarser sieving and the difference in amount gives an indication of the strength of the particles. Sample L4 behaves noticeable different from the other samples in the sense that it has much more material on the larger sieves. Samples L1, L2 and L3 have more than 60% (often more than 70%) of the material in sizes smaller than 250μm after the first gentle sieving (and this increases to more than 90% after the coarse sieving), Figure 4 and Figure 5. However, sample L4 show a totally different characteristics with more than 75% of the material in sizes larger than 250 μm after the first fine sieving. After the coarse sieving, the amount of small particles (less than 250 μm) is increased but it is still less than 50% in most experiments.

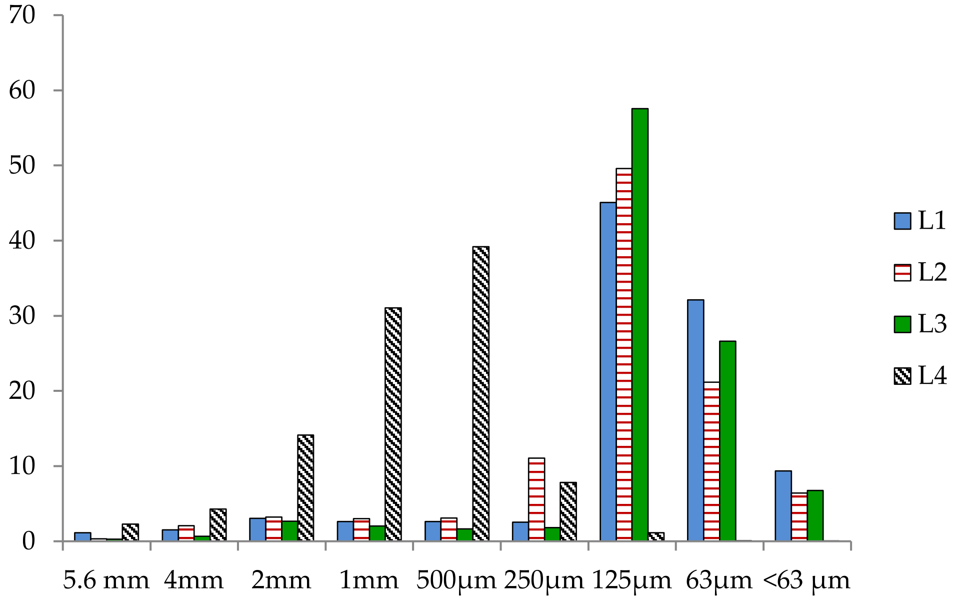


Figure 4. Comparison of particle size distribution between the different used lime mud samples after fine sieving at a heating rate of 10 K/min and maximum temperature of 850°C

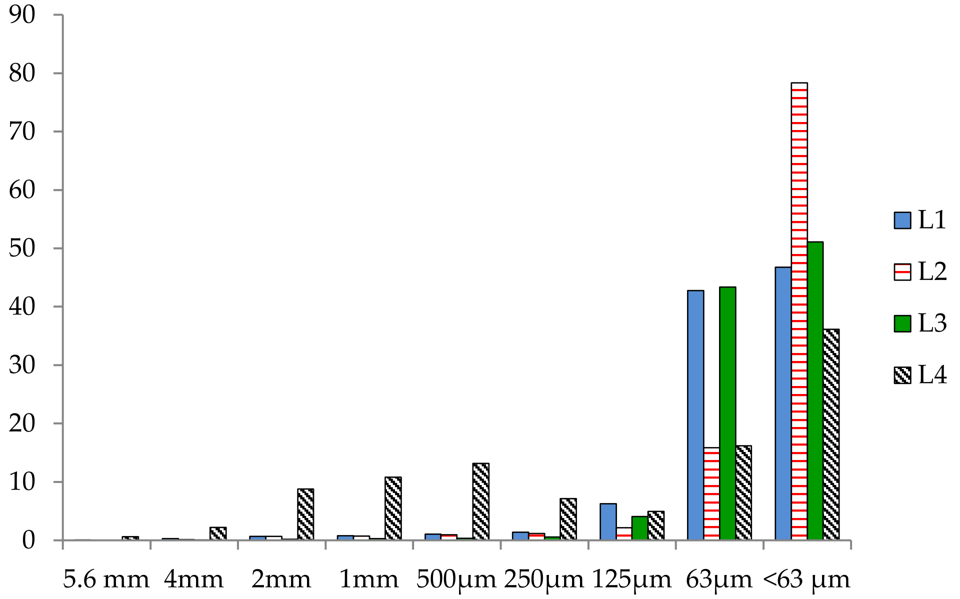


Figure 5. Comparison of particle size distribution between the different used lime mud samples after coarse sieving at a heating rate of 10 K/min and maximum temperature of 850°C

For sample L1, the particles calcined and sintered at 850°C, using a heating rate of 5 K/min, had more agglomerates (fewer fines) after the coarse sieving compared to the higher heating rates. This is an indication on rather stable particles. However, that amount of particles in the range between 63 and 125 µm increased noticeable which means that the larger particles still degraded but not to the same full extend as in the other cases (it is the only experiment of all tested that shows this behavior). The heating rates of 10 K/min and 20 K/min did not seem to influence the weight fraction obtained after the fine sieving, Figure 6. The particle distribution after coarse sieving at 950°C resembled those of 850°C indicating that the temperature has no effect on the particle's resistance to the coarse sieving.

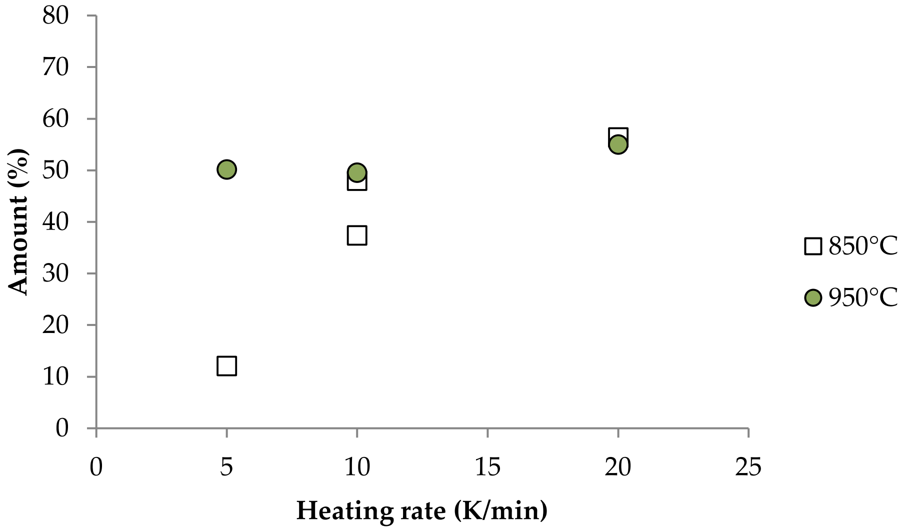


Figure 6. Amount of small particles (less than 63 µm) that are formed during coarse sieving (sample L1) in relation to the total amount of material

Sample L2, Figure 7, showed a slight difference between the stability of the particles at higher temperatures, where it seems to generate more stable particles at the higher temperature (except at the highest heating rate). This is also the sample which generates most fine particles during the coarse sieving. In sample L3, Figure 8, there is almost no difference between the tested heating rates or among the two temperatures.

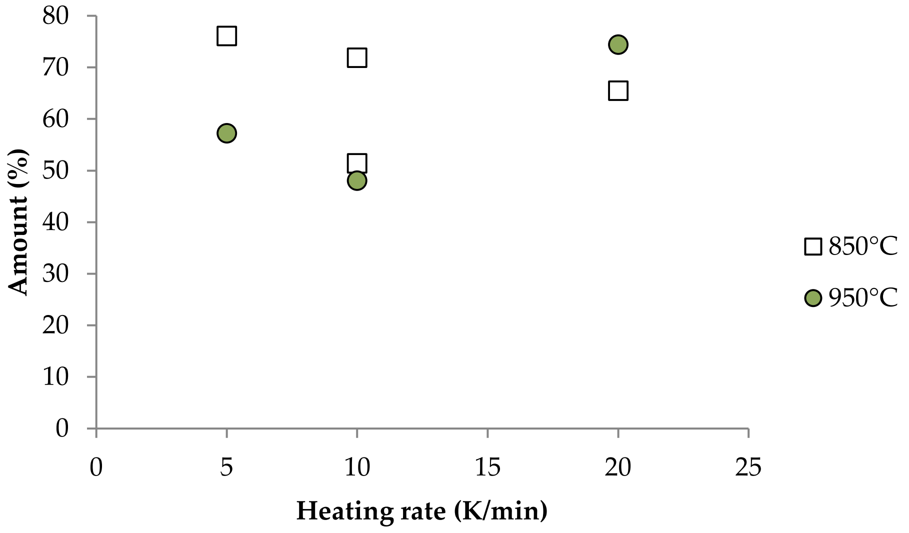


Figure 7. Amount of small particles (less than 63 µm) that are formed during coarse sieving (sample L2) in relation to the total amount of material

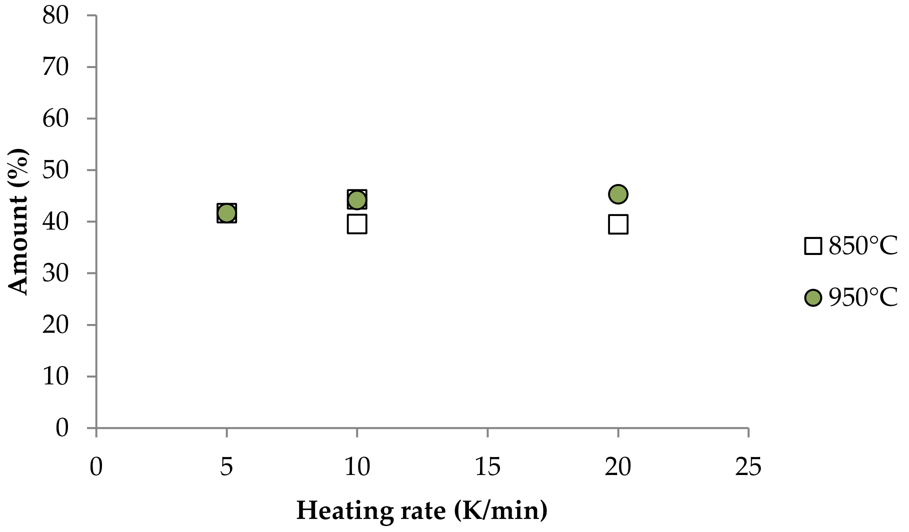


Figure 8. Amount of small particles (less than 63 µm) that are formed during coarse sieving (sample L3) in relation to the total amount of material

Sample L4 had the largest particles detected with sieving. An explanation could be that this material had the highest amount of inorganics (especially sodium) and thus were able to agglomerate at lower temperatures. However, the particles at 950°C seems to be stronger (especially for the high heating rates) as only a very small amount was detected at the smallest size fractions, Figure 9.

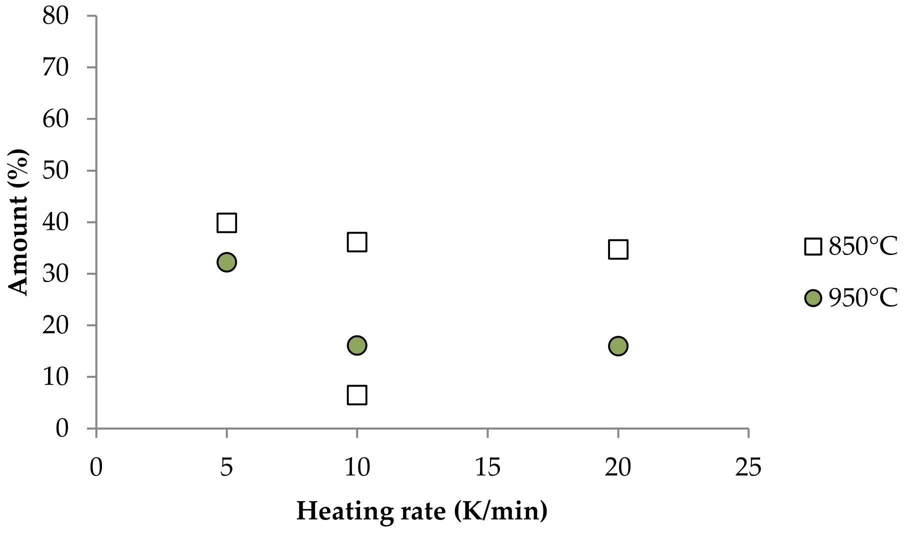


Figure 9. Amount of small particles (less than 63 µm) that are formed during coarse sieving (sample L4) in relation to the total amount of material

3.3 CALCINATION

It is observed that the reburned lime particles have calcined to a larger extent at higher heating rates (except for sample L3 which shows the highest amount of calcination and almost no difference between the heating rates), Figure 10.

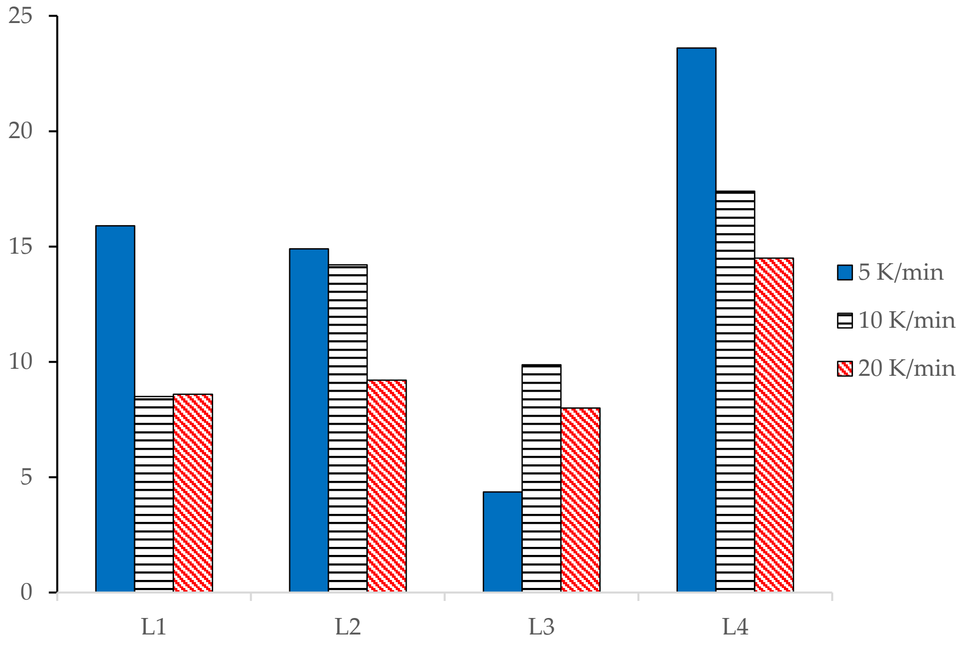


Figure 10. Amount of $CaCO_3$ in the reburned lime mud at different heating rates with 850°C as maximum temperature

This is opposite to what was expected; a lower heating rate should have given particles that were calcined to a larger extent due to the longer time above calcination temperature. One reason might be that the low heating rate gave time for increased nodule formation before the calcination which would increase the mass and heat transfer resistances and thus decrease the reaction rate. It was also indicated in the particle size distribution (and especially below 125 µm) that the particles are smaller at higher heating rate (Figure 11, Figure 12, Figure 13 and Figure 14). In sample L3 no clear size distribution difference could be detected ad it also has a more pronounced reaction at the slower heating rate.

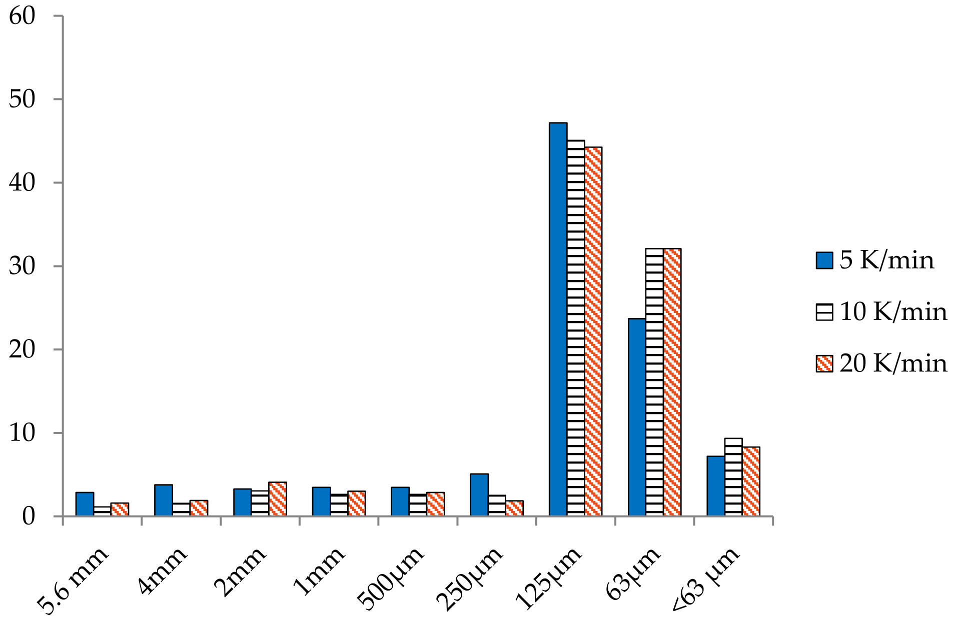


Figure 11. Particle size distribution after fine sieving for sample L1 at different heating rates

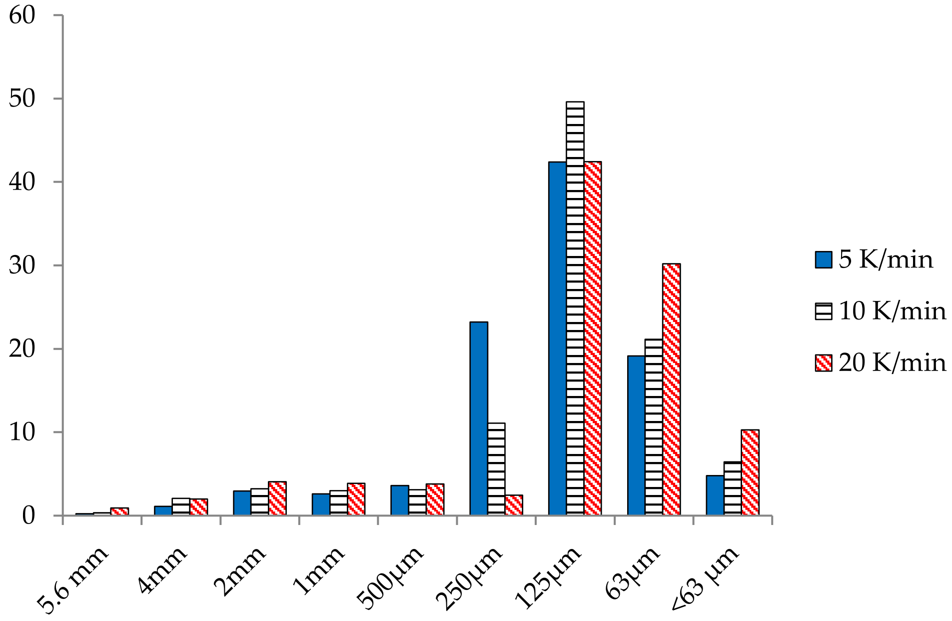


Figure 12. Particle size distribution after fine sieving for sample L2 at different heating rates

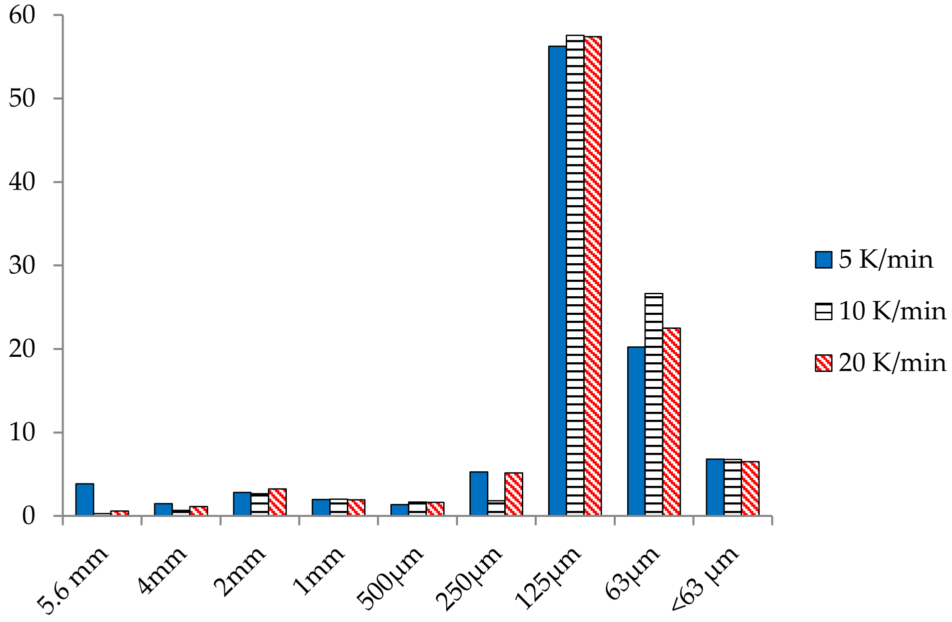


Figure 13. Particle size distribution after fine sieving for sample L3 at different heating rates

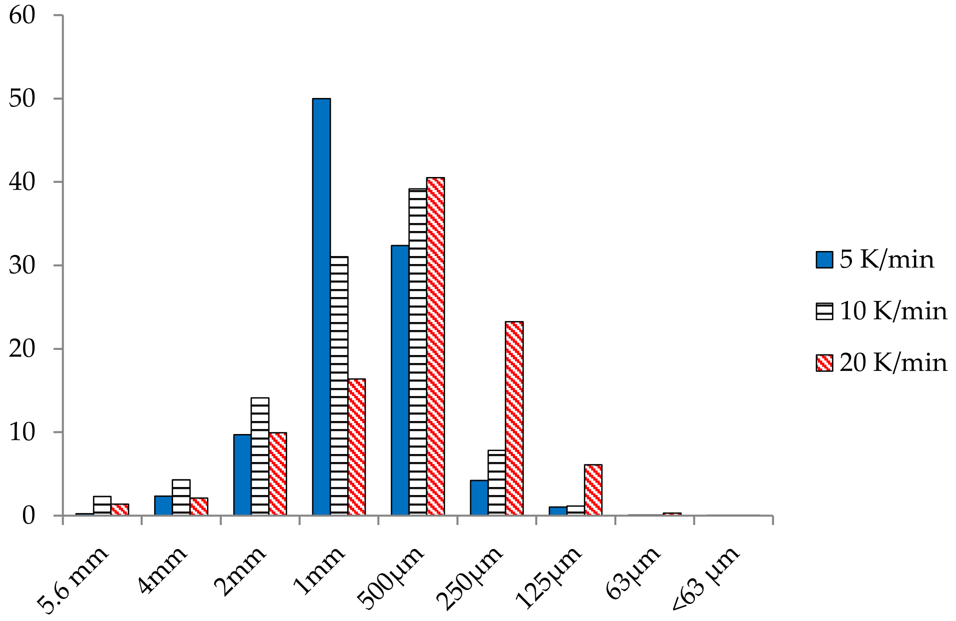


Figure 14. Particle size distribution after fine sieving of sample L4 at different heating rates

The lime particles are calcined to a higher extent at 950°C than 850°C. However, at 950°C, the lime is almost calcined to the same extent irrespective of the heating rate, Figure 15. The only difference is with sample L4 where the calcination was not completed to the same extent.

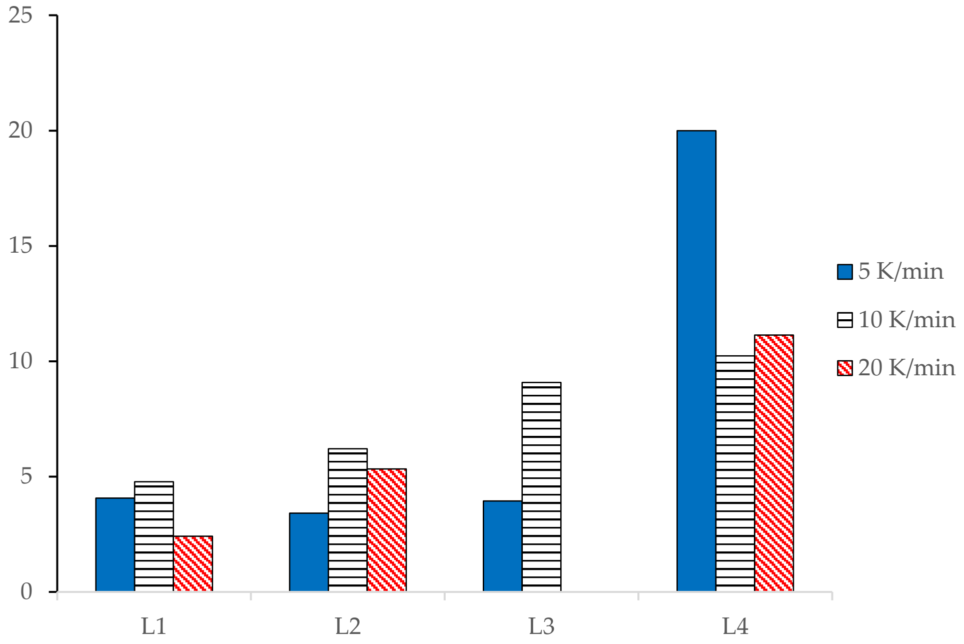


Figure 15. Amount of $CaCO_3$ in the reburned lime mud at different heating rates with 950°C as maximum temperature

3.4 THE EFFECT OF CO_2

The presence of CO_2 does not alter the weight fractions obtained after sieving (in all tests the amount of particles less than 63 μm were equal to the cases where no CO_2 was used). The increased amount of CO_2 has however hindered calcination as expected and the amount of remaining $CaCO_3$ was around 30% in samples L2-L4 at 850°C. Sample L1 was an exception where there only was a small difference compared to the original sample and the amount of residual carbonate was 12%. Most likely this is due to some problems with the CO_2 supply in this experiment. A trend was that more material in the rotary kiln gave less carbonization which then would be due to increased mass and heat transport and higher local partial pressure of CO_2.

3.5 SPECIFIC SURFACE AREA

The specific surface area (B.E.T. area) can be used as an indication of particle strength. According to Lindblom and Theliander (2001), it is expected that a smaller specific area results in a higher strength (in their investigation samples with the same partial pressure of CO_2 are compared at different residence times). In our experiments, we had the same residence time and varied the heating rate, lime mud origin, maximum temperature, and the partial pressure of CO_2. However, it was only possible to perform analyses on the variation of heating rates and lime samples. Regarding the variation in maximum temperature and partial pressure of CO_2 only a few analyses were performed (one comparison for the maximum temperature and two comparisons for the CO_2 partial pressure). The main focus of the study is the dusting on the lime kiln due to different heating rates and thus, these samples were only performed for a comparison.

Table 6. B.E.T. surface area (m^2/g) at different heating rates.

Heating rate	L1	L2	L3	L4
5 K/min	1.93	2.64	3.88	1.6
10 K/min	0.98	2.98	3.18	1.38
20 K/min	0.81	0.71	1.23	1.12

The indication here is that a higher heating rate gives a smaller surface area. This would then indicate that the particles at higher heating rates are stronger. It should be noted that the measurements of sample L1 (heating rate 10 and 20 K/min) and sample L2 (heating rate 20 K/min) were performed at a different equipment (Micromeretics TriStar). Regardless, samples L3 and L4 have been performed with the exact same condition and show a similar behavior.

Changing the partial pressure of CO_2 from 0 to 20 kPa gave two different behaviors for the two analyzed samples (L1 and L4). Sample L1 got a specific surface area (m^2/g) of 0.98 and 0.96 for the two gas compositions at a heating rate of 10 K/min and a maximum temperature of 850°C. Sample L4 showed a decrease in specific surface area when the partial pressure of CO_2 was increased. The specific surface area decreased from 1.38 to 0.54 m^2/g.

Temperature affects the surface area a great deal. Increasing the maximum temperature to 950°C increased the surface area from 1.38 to 3.93 m^2/g for sample L4 (heating rate 10 K/min).

3.6 EFFECT OF ROTATIONAL SPEED

A single test was performed to investigate whether the rotational speed had any major influence on the particle size distribution. The test was performed with the higher amount of solid material (600 g), a heating rate of 10°C/min and a maximum temperature of 850°C using either 1 rpm or 2 rpm. A higher rotational speed could mean more physical interaction and thus generate smaller particles. On the other hand it also means more chances of collisions with other particles and formation of larger agglomerates. It was however a very small difference in this single test between the two options, Figure 16, and no clear indications could be seen.

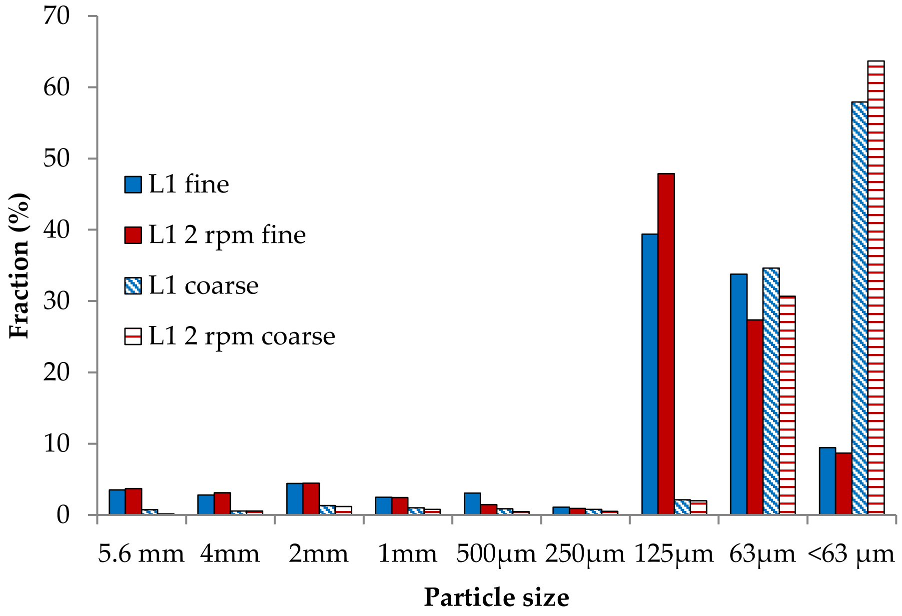


Figure 16. Particle size distribution at different rotational speed

4 Discussion

4.1 COMPOSITION OF THE LIME MUD

Sintering of lime mud is influenced by the presence of additional compounds in the lime mud. The ions as well as the melting point of the compound are important in determining the effect its presence has on the sintering. Compounds whose melting points are in the range of the sintering and calcination temperatures found in the lime kiln are more likely to enhance the sintering of the lime particles. During the kraft recovery process, the lime mud comes in contact with sodium in the liquor and sodium compounds (most likely in the form of sodium sulfate (Na_2SO_4)) are typically the largest impurity in the lime mud (Tran, 2007). Sodium compounds have a low melting point. The melting point of pure Na_2SO_4 is 884°C.

The effect of sodium compounds on the sintering of calcined lime mud has previously been studied (Lindblom 1999). Sodium carbonate, sodium sulfate and sodium phosphate were all found to increase the rate of sintering of the lime mud. The presence of sodium phosphate had a very small effect on the sintering of the calcined lime while sodium carbonate had the highest impact on the sintering,

From the lime mud composition, listed in Table 2, it can be noticed that the sodium content is highest in sample L2 and lowest in sample L1. Consequently, lime L2 is expected to sinter the most but this lime also had the smallest particle size distribution of the ordinary lime mud samples (sample L4 from the ESP dust contains even higher amounts of sodium and has an even smaller particle size distribution).

The results of the sieve analysis for all the samples have been compiled in Table 7 and Table 8. They show the % weight of particles that have not passed through the 250 μm sieve for the various lime samples after fine and coarse sieving respectively.

Table 7: Weight fraction of the reburned lime in the sieves (> 250μm) after fine sieving.

Heading rate	**Gas used**	**L1 (wt. %)**		**L2 (wt. %)**		**L3 (wt. %)**		**L4 (wt.%)**	
(K/min)		**850°C**	**950°C**	**850°C**	**950°C**	**850°C**		**850°C**	**950°C**
5	N_2	22	31	34	38	17	29	87	95
10	N_2	15±1	19	23	29	13±4	21	77±1	95
10	N_2,CO_2	16	N. A	32	N. A	15	N. A	94	N. A.
20	N_2	15	16	16	17	14	18	80	95

Table 8: Weight fraction of the reburned lime in the sieves (> 250μm) after coarse sieving

Heating rate	**Gas used**	**L1 (wt. %)**		**L2 (wt. %)**		**L3 (wt. %)**		**L4 (wt. %)**	
(K/min)		**850°C**	**950°C**	**850°C**	**950°C**	**850°C**	**950°C**	**850°C**	**950°C**
5	N_2	4	4	2	7	1	1	33	35
10	N_2	4±0	7	3±0	10	1±0	4	40±8	57
10	N_2,CO_2	4	N. A	9	N. A	2	N. A	65	N. A.
20	N_2	7	4	7	5	2	4	53	65

On comparing the amount of fines obtained after fine sieving (Table 7), it can be noticed that the sample L2 gives the largest amount of agglomerates (the smallest amount of fines) of the ordinary lime samples at both 850°C and 950°C for the heating rates of 5 K/min and 10 K/min. This might be due to the higher concentrations of sodium present in the sample as compared to the other lime mud samples. It is also to be noted that the highest difference in the weight fraction observed between these samples is at the lower heating rates of 5 K/min and 10 K/min, while at 20 K/min, the samples show similar agglomeration.

Sample L4 (ESP dust) has the highest sodium content with 2.13 % TS of Na_2O. This is double the amount of sodium found in the second highest sample (sample L2 with 1.06 %TS of Na_2O). Therefore, this sample is expected to sinter the most. The calcined and sintered ESP dust formed the largest agglomerates and was the most resistant to the forces in the coarse sieving.

4.2 EFFECT OF PARTICLE SIZE

Lindblom and Theliander (2001) found that the size of the particle/particle agglomerates is an important parameter during sintering. Smaller agglomerates sinter better than larger agglomerates due to the homogeneous heating. Therefore, smaller balls are expected to have a higher strength (it should however be remembered that the allowed time for sintering at 850 °C is only 1 hour in these experiments and the referred study used a longer residence time at this temperature).

In the current study, sample L4 had the smallest initial particle size but gave the largest amount of agglomerates both after the fine and the coarse sieving. One explanation for this might be that the particles have sintered and agglomerated at a faster rate (at lower temperatures) due to the sodium compounds present. The melted sodium might have initially caused the formation of $CaCO_3$ agglomerates. With increased temperature, similar to the hot end in the real lime kiln, it is likely that the surface of these agglomerates are calcined to CaO and further sintered leading to stronger particles. The findings are supported by the findings that sample L4 had the largest amount of residual carbonate when compared with the other samples at similar condition (Figure 10 and Figure 15).

4.3 SPECIFIC SURFACE AREA

One hypothesis before starting the project was that the dusting within a lime kiln would enhance further dusting due to a shift in impact from the flame section because less radiation would pass through to the lime at the wall and instead heat up the small dust particles that in its turn would be very hard sintered. The dust particles might proceed with the gases further back in the kiln and thus act as a heat load and increase the heating rate of the incoming lime mud. If particles start to agglomerate and sinter before all calcination has finished that might have two different effects. One is that the particles might have too large amount of remaining carbonate and thus act as a dead load in the cycle. The other effect is that since the agglomerates are formed before the calcination is complete, this will yield a weaker agglomerate (reburned lime mud has lower molar volume compared to lime mud and thus this transformation will affect the strength of the agglomerate).

Another aspect was how the load in the lime kiln would impact the dusting. A high load would mean a slower initial heating rate of the lime mud (more material to be heated combined with a lager degree of filling in the kiln) but where the flame intensity would be larger (more fuel is needed) and thus give a higher heat transfer at the highest temperatures. Depending on the heat balances in the oven the period of high heat transfer to the lime mud could either increase the effective heating rate during agglomeration and could lead to larger agglomerates before the calcination occurs (risk of having weak particles).

In our case, it is seen that higher heating rate generate smaller surface area and thus it would mean stronger agglomerates. However, this was not something that could be confirmed (Figure 6 to Figure 9) with the sieving tests (amount of produced material by the coarse sieving) where sample L1 showed the opposite trend with more fine material at higher heating rate, samples L2 and L3 showed insignificant differences among the different heating rates and sample L4 had a tendency in line with the theory. Most samples (L1, L2 and L4) showed a larger fraction of smaller particles after the fine sieving (Appendix B) which is an indication of the particle size in the oven. It should be remembered that the analysis of the specific surface area is on particles between 1 and 2 mm and the majority of the material is smaller than this size which means that it might not be fully representative. The B. E. T. analysis was also distributed during more than 5 months and storage might as well affect the result.

5 Conclusion

The proposed investigation method in this pre-study showed to be useful and could handle the different samples. Mass balances were closed to nearly 100%.

It was observed that the lime mud samples behave differently. This was expected as the calcination and the sintering process depends on the properties of the lime mud. Therefore, the results are compiled separately in the form of separate tables for the various lime mud samples. It should be noted that the experimental conditions of using 300 g dry lime mud and a residence time of 1 hour at the final temperature might not be optimal for comparisons of the real cases and to identify the phenomenon about nodule formation, chemical reactions and sintering. However, these conditions were chosen to mimic conditions in the real lime kiln during nodule formation and initial agglomeration.

5.1 SAMPLE L1

Parameter	Particle agglomeration (particle distribution fine sieving)	Stability (Particle distribution coarse sieving)	% of calcination
Heating rate	No effect observed	Only a small amount of fines were produced at 5K/min (probably an outlier).	Higher heating rates improves calcination at 850°C
CO_2	No effect observed	No effect observed.	Hindered calcination.
Temperature	The higher temperature is seen to result in fewer fines (more agglomeration) at heating rate of 5K/min.	No effect observed.	Increased calcination at higher temperature.

5.2 SAMPLE L2

Parameter	Particle agglomeration (particle distribution fine sieving)	Stability (Particle distribution coarse sieving)	% of calcination
Heating rate	More fines produced as the heating rate increases.	Unclear	Higher heating rates improves calcination at 850°C
CO_2	Presence of CO_2 resulted in larger particles	Slight decrease in the amount of fines (more stable particles)	Hindered calcination.
Temperature	A higher temperature results in more agglomerated particles for the 5 and 10K/min heating rates.	The amount of fines are similar at the 2 temperatures	Increased calcination at higher temperature.

5.3 SAMPLE L3

Parameter	Particle agglomeration (particle distribution fine sieving)	Stability (Particle distribution coarse sieving)	% of calcination
Heating rate	Increase in the number of fines as the heating rate is increased (only at 950°C)	No observed effect.	No effect observed
CO_2	No effect observed	A slight reduction in percentage of fines	Hindered calcination.
Temperature	The higher temperature is seen to result in fewer fines for the 5K/min heating rate.	No observed effect	No observed effect. It had a high degree of calcination at 850°C.

5.4 SAMPLE L4

Parameter	Particle agglomeration (particle distribution fine sieving)	Stability (Particle distribution coarse sieving)	% of calcination
Heating rate	Larger particles than any other samples. Almost no particles less than 63 µm.	Higher strength observed with faster heating rate.	An increase in the calcination with the heating rate
CO_2	Higher agglomeration	Higher strength observed with the addition of CO_2	Two tests gave different results.
Temperature	Increased temperature resulted in more agglomerated particles	More stable particles at increased temperature.	Increased calcination at higher temperature.

Increasing the heating rate results in more fines but the difference is rather small. This might be a reinforcement of the problem as more dust would shift the temperature profile and transfer more energy further back in the kiln and thus increase the heating rate. Regarding the calcination, there is a trend between the extent of calcination and the heating rate at 850°C but the trend is not so clear at 950°C (partly depending on a higher degree of calcination).

6 Future suggestions

It is clear that the performed study is a pre-study. There are indication of impact of particle strength due to changes in lime kiln conditions and lime mud composition but the study is not complete to make clear relations between the effects and the conditions. There are a couple suggestions for further studying the concept

6.1 EXPERIMENTAL EQUIPMENT

The current study was performed with a relatively small amount of solid material (300-600 g) and this will not give the same conditions as the real lime kilns (almost all material has contact with the metal surface in the pilot lime kiln whereas this is not the case in the actual running process where the degree of filling could be around 10%). A larger amount could be used in the experimental set-up but that would require a slight modification of the equipment in order to hinder the material from moving out to the sides where the temperature is colder. A longer residence time would be beneficial as the amount of agglomerates were quite low and the amount of residual carbonate rather high (above 8% for all samples at 850°C except for sample L3 which was significant lower).

6.2 ANALYSES

It is suggested to increase the number of analyses of the material and especially surface analysis such as surface area and microscopy (SEM). Correct strength measurements would be desired (the currently used method by having fine and coarse sieving is merely an indication)

6.3 NUMBER OF EXPERIMENTS

As this was a pre-study, only a limited number of experiments were performed and focus was on covering a large area (several lime mud samples and heating rates) while the number of repeating experiments was reduced to a minimum (one condition for each lime mud).

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Bilaga A: Particle size distribution results

Appendix A list the result from fine and course sieving for all experiments. The actual condition and sample for each test is found in Table 5 (section 2.2.3).

Table A1. Particle size distribution after fine sieving for all experiments

Sample No	5.6 mm	4mm	2mm	1mm	500 µm	250 µm	125 µm	63µm	<63 µm
1	2,85	3,78	3,29	3,46	3,46	5,08	47,18	23,69	7,21
2	0,33	2,05	3,23	3,00	3,11	11,08	49,60	21,15	6,44
3	1,58	1,90	4,10	3,02	2,85	1,87	44,25	32,11	8,31
4	0,24	2,35	9,71	49,98	32,38	4,22	1,03	0,08	0,01
5	0,93	2,00	4,06	3,88	3,79	2,44	42,45	30,18	10,28
6	2,29	4,30	14,13	31,03	39,19	7,81	1,14	0,08	0,03
7	1,13	1,54	3,05	2,63	2,61	2,53	45,05	32,10	9,36
8	1,38	2,12	9,92	16,40	40,52	23,26	6,10	0,29	0,02
9	0,22	1,11	2,95	2,59	3,61	23,20	42,38	19,15	4,79
10	1,97	2,33	3,89	2,75	2,19	2,76	49,48	27,19	7,44
11	0,95	1,68	9,57	19,92	36,42	26,20	5,17	0,08	0,00
12	4,10	1,28	2,43	2,14	4,35	19,99	38,76	21,55	5,40
13	1,49	4,58	17,15	30,11	40,16	5,60	0,85	0,05	0,00
14	6,66	4,97	6,31	3,47	2,20	1,60	37,09	29,64	8,06
15	3,50	2,81	4,41	2,48	3,07	1,09	39,39	33,80	9,46
16	3,68	3,13	4,45	2,43	1,44	0,92	47,88	27,38	8,70
17	5,89	4,09	5,90	4,54	3,73	7,40	35,87	24,73	7,86
18	0,06	1,05	3,62	2,96	3,05	11,97	51,03	20,56	5,70
19	0,73	3,11	19,93	32,42	38,11	4,71	0,60	0,39	0,00
20	0,26	0,66	2,66	2,02	1,64	1,81	57,57	26,62	6,76
21	0,57	1,11	3,24	1,92	1,61	5,13	57,41	22,51	6,51
22	3,84	1,46	2,81	1,98	1,35	5,26	56,25	20,24	6,81
23	2,23	1,67	3,43	2,61	1,90	3,91	56,75	21,40	6,11
24	1,50	2,71	2,35	1,72	1,40	7,45	60,85	17,55	4,48
25	0,14	1,70	3,51	3,34	6,66	22,76	41,25	16,83	3,80
26	1,68	3,52	4,61	3,17	2,98	3,19	44,72	27,19	8,94
27	2,63	3,31	4,63	2,81	2,15	2,39	52,22	23,04	6,82
28	0,60	3,04	7,67	14,89	60,66	11,67	1,41	0,06	0,00
29	0,50	2,36	12,56	27,25	45,39	10,26	1,62	0,07	0,00
30	0,47	2,55	2,45	2,73	3,04	5,90	38,39	32,90	11,59
31	1,42	3,54	5,16	3,13	2,51	15,41	46,54	18,13	4,17
32	1,29	2,18	11,61	31,55	39,38	11,96	1,98	0,05	0,00
33	2,18	3,85	5,29	3,07	2,26	4,46	54,74	19,37	4,78
34	4,85	2,64	2,48	1,80	1,60	15,52	53,95	14,51	2,65
35	2,19	4,87	8,46	4,62	4,39	3,04	17,64	43,14	11,64
36	1,55	2,82	4,85	4,11	5,84	9,99	40,49	21,02	9,34
37	1,95	3,56	3,85	2,55	2,00	1,39	50,60	25,94	8,15
38	0,79	1,33	13,78	31,90	32,89	15,86	3,20	0,26	0,00

Table A2. Particle size distribution after coarse sieving

Sample No	5.6 mm	4mm	2mm	1mm	500µm	250µm	125µm	63µm	<63 µm
1	0,00	0,04	0,26	0,77	1,17	1,98	8,93	67,55	19,30
2	0,00	0,11	0,70	0,73	0,97	1,18	2,15	15,85	78,31
3	0,58	0,61	1,50	1,33	1,42	1,55	2,31	26,01	64,68
4	0,11	0,83	6,10	7,69	7,93	5,78	4,86	26,86	39,85
5	0,10	0,54	1,34	1,44	1,57	1,51	1,79	15,92	75,78
6	0,61	2,21	8,80	10,82	13,18	7,15	4,95	16,17	36,11
7	0,04	0,27	0,68	0,76	1,03	1,38	6,29	42,79	46,76
8	0,91	1,39	7,47	13,49	12,01	9,76	7,88	12,41	34,69
9	0,03	0,02	0,13	0,30	0,46	0,64	1,67	15,89	80,85
10	0,05	0,29	1,07	0,93	0,82	0,90	3,12	35,26	57,56
11	0,32	0,82	7,15	13,25	15,94	7,83	5,84	12,13	36,73
12	2,62	1,00	1,75	1,69	1,49	1,26	1,02	36,92	52,25
13	1,06	3,10	13,47	19,22	15,80	5,98	5,52	21,06	14,77
14	0,68	1,26	2,33	1,56	1,15	1,14	3,64	30,53	57,72
15	0,73	0,58	1,31	1,02	0,86	0,78	2,13	34,65	57,95
16	0,16	0,57	1,17	0,79	0,48	0,50	1,99	30,66	63,68
17	0,55	0,90	1,97	1,81	1,96	2,03	3,81	26,29	60,68
18	0,00	0,06	0,27	0,63	0,96	1,22	3,88	35,91	57,09
19	0,36	0,99	10,68	20,68	16,63	6,31	13,64	24,26	6,46
20	0,00	0,02	0,20	0,31	0,34	0,56	4,08	43,39	51,10
21	0,00	0,13	0,55	0,40	0,33	0,52	5,23	46,80	46,04
22	0,00	0,00	0,01	0,07	0,18	0,41	7,11	43,71	48,50
23	0,05	0,06	0,37	0,40	0,39	0,73	10,53	48,13	39,34
24	0,00	0,05	0,11	0,38	0,13	0,32	8,33	46,65	44,04
25	0,00	0,05	0,21	0,82	2,50	3,79	4,89	26,71	61,03
26	0,00	0,26	1,29	1,60	1,34	2,32	3,84	30,88	58,48
27	0,23	0,41	1,12	0,74	0,73	1,13	4,08	39,41	52,15
28	0,19	1,17	4,33	8,54	14,28	6,69	8,31	24,24	32,25
29	0,08	1,50	8,32	17,12	21,81	8,02	6,48	20,56	16,11
30	0,17	0,25	0,50	0,76	1,32	1,88	1,73	7,38	86,01
31	0,00	0,42	1,27	0,84	0,80	1,10	4,13	37,12	54,31
32	0,47	1,55	8,38	24,41	21,35	9,00	4,89	13,94	16,00
33	0,13	0,20	1,20	0,81	0,68	1,01	6,12	40,85	48,99
34	0,00	0,00	0,02	0,05	0,41	0,63	8,63	45,90	44,37
35	0,29	1,92	3,97	2,28	3,34	3,17	1,88	13,64	69,50
36	0,00	0,44	1,12	1,11	2,98	3,44	3,97	29,56	57,39
37	0,47	0,72	1,16	0,60	0,54	0,71	2,58	37,06	56,17
38	0,31	0,87	8,26	24,79	22,33	8,11	7,00	7,71	20,61

Bilaga B: Particle size distribution at different heating rates

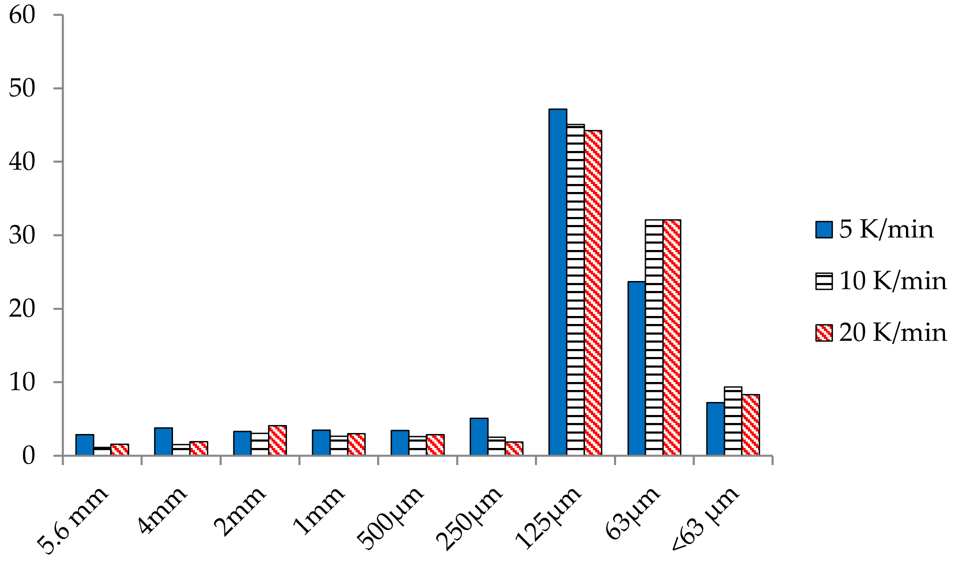

Figure B 1. Sample L1 fine sieving

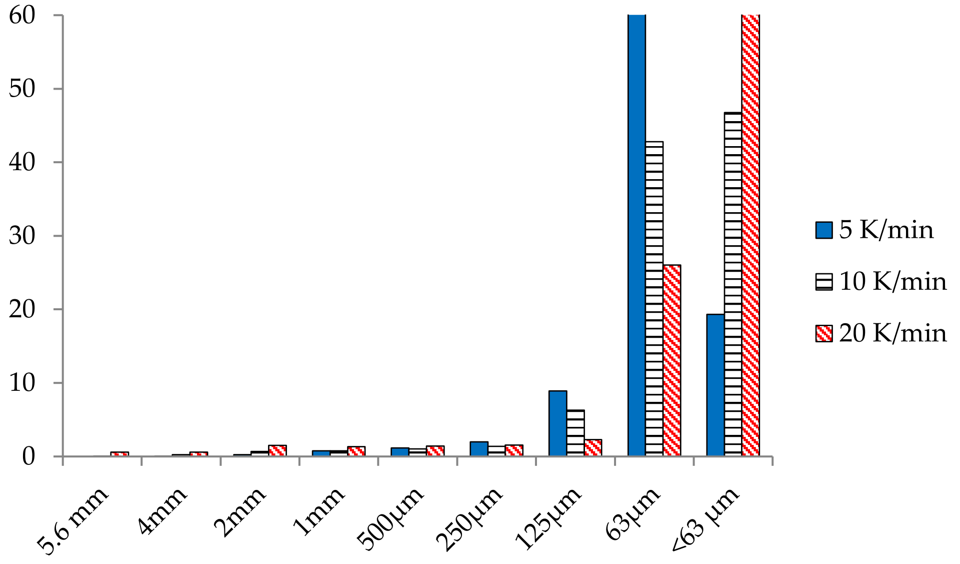

Figure B 2. Sample L1 coarse sieving

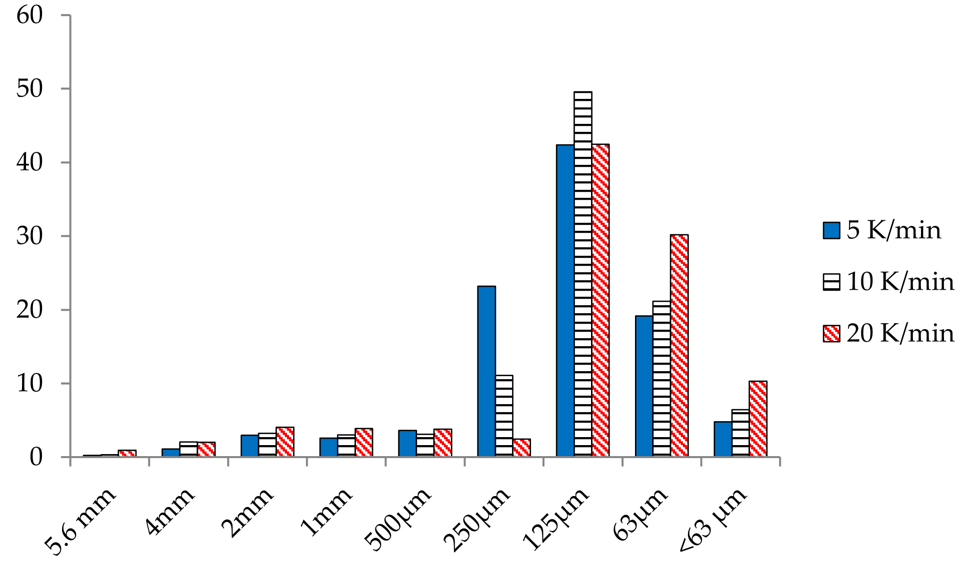

Figure B 3. Sample L2 fine sieving

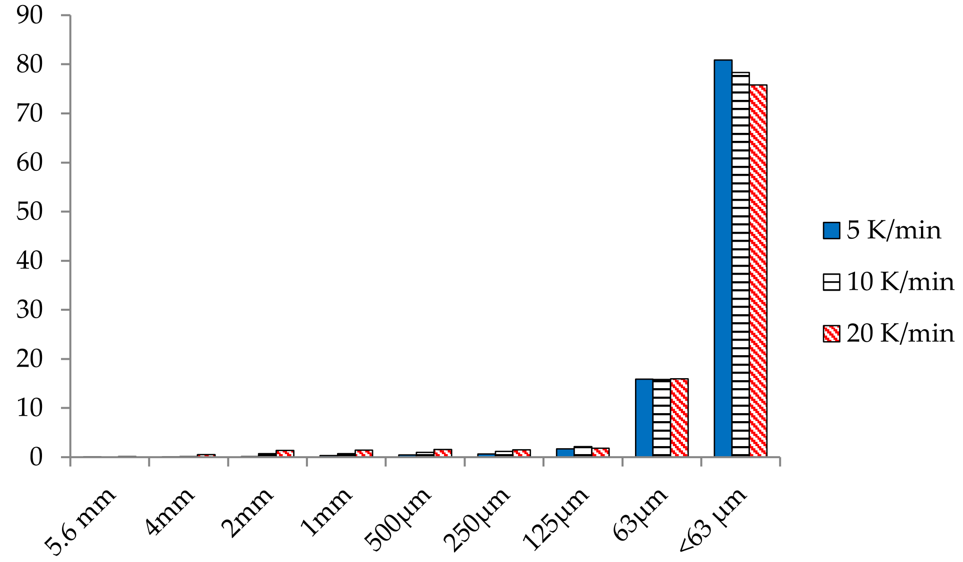

Figure B 4. Sample L2 coarse sieving

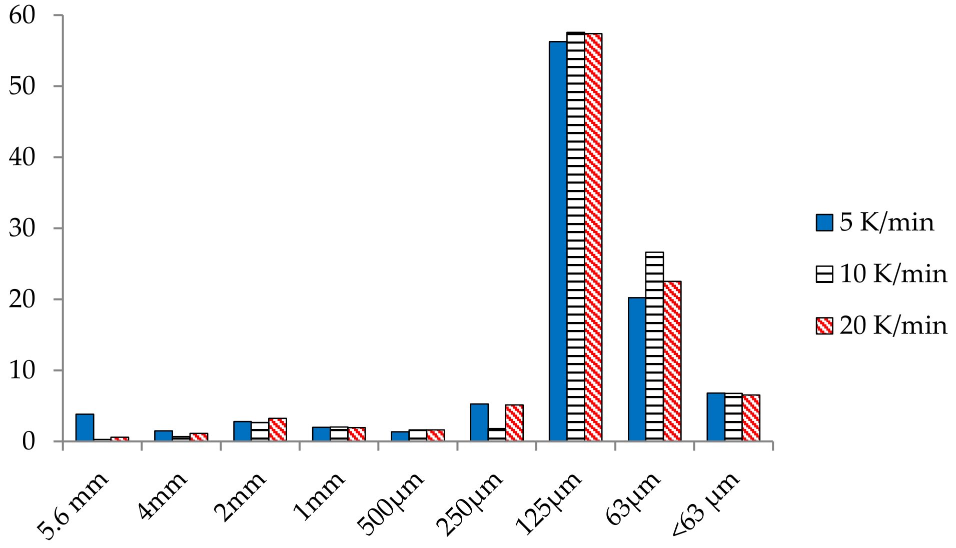

Figure B 5. Sample L3 fine sieving

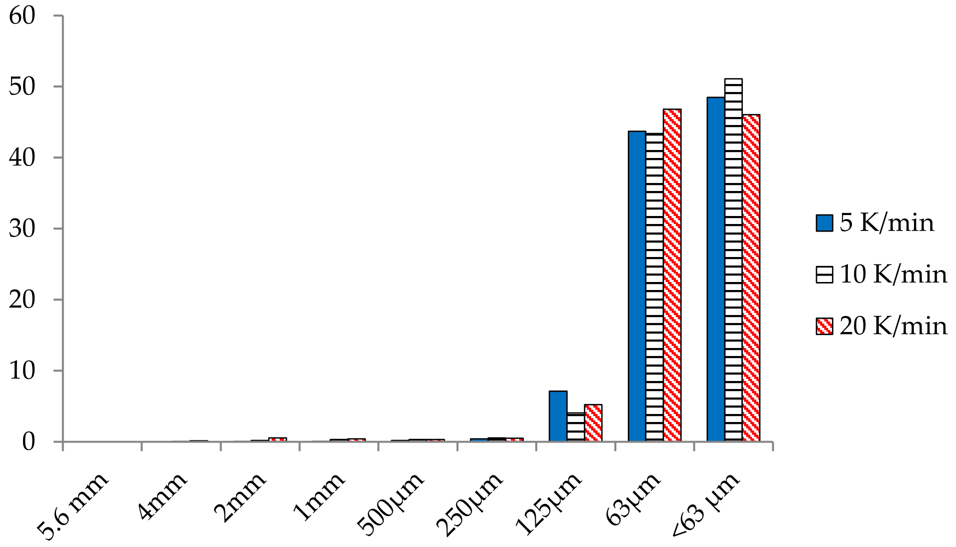

Figure B 6. Sample L3 coarse sieving

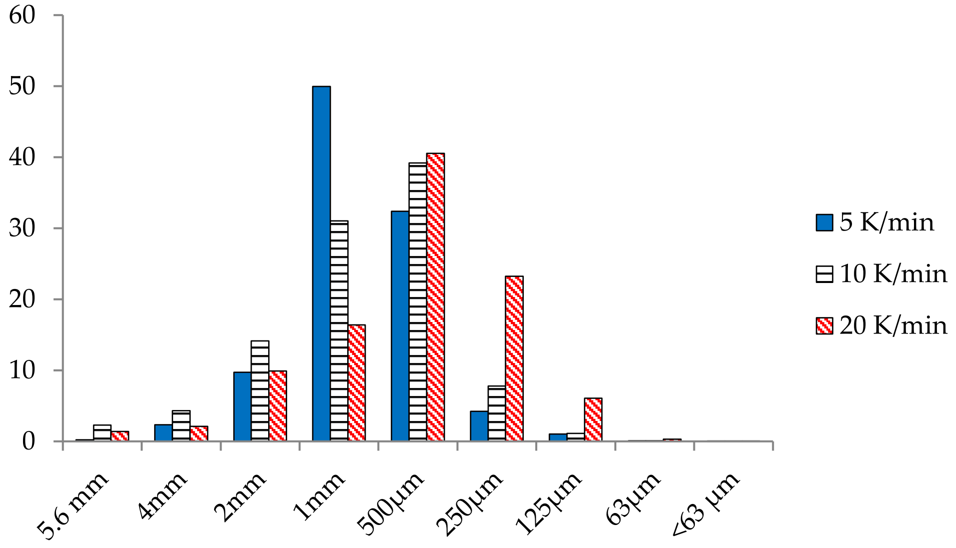

Figure B 7. Sample L4 fine sieving

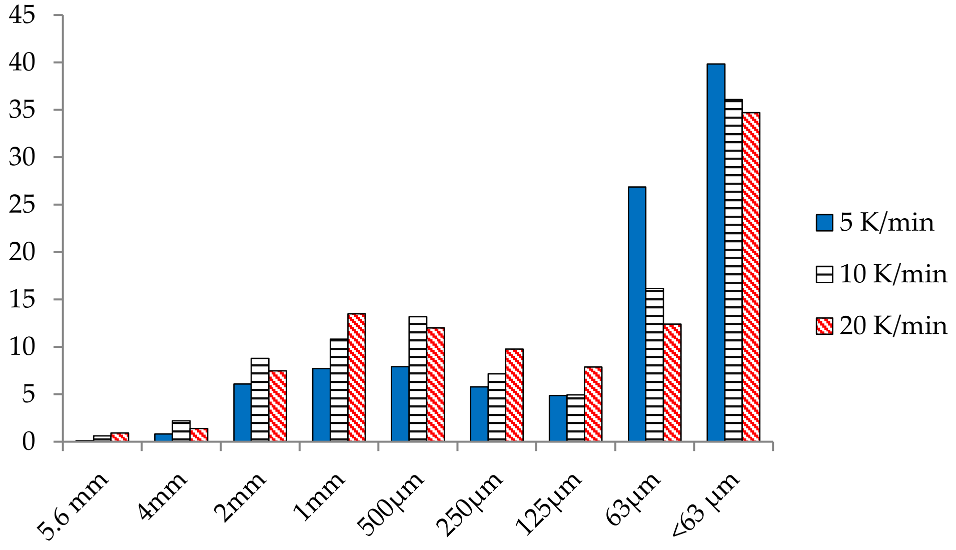

Figure B 8. Sample L4 coarse sieving

LIME KILN DUSTING

Dusting in a lime kiln can seriously affect the performance of the kiln which may lead to increased fuel consumption or reduced production.

In this study, the heating rate as main parameter has been investigated with its relation to particle strength and size distribution. Four different lime samples were tested; three ordinary lime muds and one lime sample from the electrostatic precipitator.

Carbon dioxide affected the degree of calcination negatively but had only a small impact on the particle size distribution. It was a tendency that a higher heating rate gave more particles in the smaller size fractions which might increase the severity of lime kiln dusting as heat is transferred further back in the oven with the sensible heat of the dust particles and thereby increase the heating rate.

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