The Influence of Carbon Dioxide on Ring and Ball Formation in a Pilot-Scale Rotary Kiln

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Abstract

The influence of carbon dioxide on ring and ball formation in a pilot-scale rotary kiln has been investigated. The balls were found to have a higher specific surface area and a higher content of residual carbonate compared with the rings and dusts: this was probably due to a lower heat transfer rate. The influence of carbon dioxide on sintering proved to be different for the two lime muds investigated. One of them reached a minimum in specific surface area at about 10 weight-% and the other decreased its specific surface area with increasing residual carbonate. The strength of the balls increased with increasing residual carbonate. At constant temperature and partial pressures of carbon dioxide, the strength of the balls increases with time and the specific surface area decreases.

Introduction

Lime mud reburning is one of the steps in the chemical recovery process in the kraft pulp mill. The reburning of lime mud is normally carried out in a rotary kiln. The rotating kiln is a long cylindrical furnace which is somewhat inclined to make it a continuous process (Figure 1). The moist lime mud is fed in at the upper end and, on its way down through the kiln, is dried, heated and calcined. Fuel is combusted at the lower end of the kiln and hot flue gases leave the kiln at the upper end, thus making the kiln a counter-current direct heat exchanger. During calcination, the calcium carbonate dissociates into calcium oxide (lime) and carbon dioxide. The porous lime also sinters because of the high temperature in the kiln. During sintering, the solid material may harden significantly, and rings and balls often form in the kiln. Ring and ball formation is a persistent problem in many mills and can easily affect the production capacity. In severe cases, it can also be the cause of shut-downs in order to clean the kiln. The results of an inquiry sent to all Swedish kraft pulp mills showed that ring formation was a real problem encountered by many mills (about 70%), and that they often did not know the cause of the problems.

The sintering atmosphere in a rotary kiln contains carbon dioxide, since hot flue gases supply the heat needed for calcination. Tran et al. (1992) and Skrifvars et al. (1992) studied the inter-particle gas-solid chemical reaction sintering as a mean of forming and hardening rings in rotary kilns. It was found in both studies that recarbonation is the most important mechanism in hardening mid-kiln rings (which are the most common and troublesome type of rings). The calcination reaction is reversible and recarbonation occurs when the temperature is lower than the equilibrium temperature. The mid-kiln rings are formed close to the maximum temperature where CaCO₃ (s) is still thermodynamically stable, which is, consequently, in the middle of the kiln (at the very end of the heating zone and the beginning of the calcination zone), where the concentration of carbon dioxide is high and the temperature not too high. Experimentally, Tran et al. (1992) and Skrifvars et al. (1992) calcined lime mud and limestone, respectively,

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and then shaped cylindrical pellets, which were heat-treated in different temperatures and atmospheres. Sintering was measured as the compressive strength of the sintered pellets. The strength measured after recarbonation was by far the highest compared with the strengths obtained when using SO₂, O₂ and H₂O in the atmosphere (Skrifvars et al. 1992) or when doping the lime mud with different impurities (Tran et al. 1992); neither did high-temperature sintering yield as hard pellets (Tran et al. 1992). Tran et al. (1992) found that the relationship between the compressive strength and degree of recarbonation was linear, independent of reaction time, temperature and conditions at which the pellets had been treated.

The influence of carbon dioxide on the intra-particle sintering of calcined lime mud was investigated earlier by Lindblom et al. (1996). The sintering equipment was a quartz glass reactor, and a small sample of lime mud was placed on a fritted disc of quartz glass. Hot gases with different mixtures of nitrogen and carbon dioxide flowed through the solid, and the intra-particle sintering was determined by measuring the specific surface area. It was found that carbon dioxide strongly enhanced sintering, since it affected the decrease of the specific surface area. At equilibrium, the specific surface area decreased even more, probably due to recarbonation as well as sintering.

The objective of the current study was to investigate how the partial pressure of carbon dioxide in the sintering atmosphere influences the formation of rings and balls. This was done in a pilot-scale rotary kiln, where dried lime mud was treated at different temperatures in varying concentrations of carbon dioxide. Sintering was determined by measuring the specific surface area and, in addition, the strength of the formed balls was measured. The residual carbonate was also analysed.

**Experimental**

**Equipment**

The experiments were carried out in a rotary kiln with a heated length of 1125 mm and a diameter of 190 mm (Entech, Energiteknik AB). The inner tube is made of high-temperature steel (Avesta Sheffield 253 MA). Three electrical heating elements (type S) in three zones are used to heat the kiln electrically; it can be operated at temperatures up to 1000°C. The temperature is controlled with PID-controllers (Eurotherm 2116). Two extra thermocouples (Eurotherm, type N) are inserted through the ends of the kiln; they are located in the gas bulk and in the solid material, respectively. The kiln is horizontal and, consequently, a batch reactor. It can be rotated at a speed of up to 6 rpm. Both ends are partly made of quartz glass to allow for visual control, and are easily removable.

The sintering atmosphere is nitrogen with different concentrations of carbon dioxide. The two gas flows are set with flowmeters (Platon A10HS786PC and EK-EB89, Kytölä Instruments AB) and then mixed in a static mixer. The total gas flow is 20 l/min, at STP and the total pressure is 1 bar. The mixed gas is preheated in a preheater (Entech, ETF 30/12) to about 500°C before entering the rotary kiln. The outgoing gas is cooled in a heat exchanger and passes two cyclones before leaving the system.

**Lime mud**

Two different lime muds had to be used. The first one was used in the extensive series at 850°C, and the second one was used when studying the influence of temperature. The composition of the two lime muds can be seen in Table 1. The specific surface area, mean particle size, initial density and the content of
carbonate and free calcium oxide of the lime muds are shown in Table 2. SEM images were also taken to characterize the different lime muds. Figure 2 shows that their microstructures are similar.

Table 1 Composition of the dried lime muds. The elements, with the exception of calcium, are expressed as their related oxides.

<table>
<thead>
<tr>
<th>Component</th>
<th>Lime Mud I (weight-%)</th>
<th>Lime Mud II (weight-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>86</td>
<td>97</td>
</tr>
<tr>
<td>MgO</td>
<td>0.87</td>
<td>0.35</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.4</td>
<td>0.92</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>5.8</td>
<td>0.67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.28</td>
<td>&lt;0.035</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.73</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.057</td>
<td>&lt;0.058</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.18</td>
<td>0.033</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.018</td>
<td>0.0062</td>
</tr>
<tr>
<td>MnO</td>
<td>0.030</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table 2 Characteristics of the lime muds.

<table>
<thead>
<tr>
<th></th>
<th>Lime Mud I</th>
<th>Lime Mud II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²/g)</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Mean particle size (µm)</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>2646</td>
<td>2630</td>
</tr>
<tr>
<td>Carbonate (weight-%)</td>
<td>79</td>
<td>88</td>
</tr>
<tr>
<td>Free calcium oxide (weight-%)</td>
<td>0.78</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Procedure

Before heating the kiln, 2 kg of the dried lime mud was spread out evenly in the reactor. This was done through the openings in both of the ends. The ends were then mounted and it was ensured that the two extra thermocouples were positioned correctly. The gas flow was turned on and the heating of the gas and the kiln was started as well as the rotation of the kiln. The temperature increase in the gas bulk and the solid material was monitored, and it was found that it took about 1 hour for them to reach the predetermined temperature. This hour was subtracted from the total time in order to obtain the reported time.

When the experiment was over, the heating was turned off. The gas flow and rotation were continued, however, in order to achieve as rapid cooling of the solid material as possible. When the temperature had decreased to about 400°C, everything was turned off and left overnight. The following morning, the reactor was opened and the interior of the tube was inspected. Three different kinds of samples of the reburned lime mud were taken, i.e., balls, rings and powders. These were analysed with respect to carbonate and free calcium oxide. The specific surface area was measured by a five-point nitrogen adsorption method in Micromeritics Gemini 2370, and the theory of Brunauer, Emmet and Teller (Lovell and Shields 1984) was used to calculate the specific surface area. The balls were photographed and their sizes noted.

For the sintering experiments that produced hard enough balls, the compression strength of the balls was measured with a granular strength testing unit from Etewe.

The variables were temperature, sintering time and partial pressure of carbon dioxide. The temperatures
When increasing the partial pressure of carbon dioxide, which can be seen in the low residual carbonate. This is because balls were seldom present after experiments at 850°C. The partial pressure of carbon dioxide at equilibrium is a function of temperature, and was calculated with the help of an expression derived by Baker (1962). At 750°C, the partial pressure at equilibrium is 9 kPa and, at 850°C 48 kPa. Therefore, the partial pressure of carbon dioxide was chosen to vary from 0 to 60 kPa. At 950°C, the partial pressure at equilibrium is 190 kPa, which was impossible to use in the experiments since the total pressure was 100 kPa.

Results

The results were evaluated separately for dusts, rings and balls. The dusts and rings showed a similar behaviour in all aspects, while the balls behaved slightly differently in some tests. The balls generally had a larger specific surface area, and the calcination reaction was also slower, probably due to a lower heat transfer rate. In most of the graphs presented here, the results of the analysis balls are shown because, of the balls, rings and dusts, it was possible to measure the strength of the balls. The balls were chosen to be shown throughout the paper so that the strength could be compared with residual carbonate, specific surface area etc.

When comparisons between different temperatures are made, the powder, rather than the balls, is shown. This is because balls were seldom present after experiments at 750°C. It should also be remembered that during the experimental work, two different lime muds had to be used. Lime mud I was used in the first part of the study when the relationships between strength, specific surface area and residual carbonate at 850°C were investigated. In the latter part of the study, where the temperature dependence was examined, lime mud II was used. Several experiments at 850°C had to be rerun with the second lime mud for the purpose of comparing the results at different temperatures. The lime mud used is clearly indicated in each graph.

The first lime mud was used, and the temperature was 850°C, in the experiments referred to in the first part below. It is shown in Figure 3 that the degree of calcination (a higher degree is shown by a low residual carbonate) is high at partial pressures of carbon dioxide up to 24 kPa in the sintering atmosphere. The degree of calcination is high, especially longer times, which can be seen in the low residual carbonate. When increasing the partial pressure of carbon dioxide above 24 kPa, the residual carbonate increases rapidly. At partial pressures between 48 and 60 kPa, equilibrium is obtained, and the high residual carbonate is the same after five and seven hours. Only results for the balls are shown in Figure 3. It should be mentioned, though, that for constant partial pressures below equilibrium (48 kPa), the range of the residual carbonate from one to seven hours is wider for the balls than for the dusts and rings. The wider range is mainly because of the poor calcination after one hour. It can also be seen that, at all partial pressures of carbon dioxide below equilibrium, the residual carbonate decreases with increasing time but, at and above equilibrium, there is no change between five and seven hours.

![Figure 3](image-url)

When studying the change in specific surface area with the degree of calcination, two different behaviours can be observed (Figure 4). The largest specific surface areas can be found when pure nitrogen is used as the sintering atmosphere. If carbon dioxide is added up to a partial pressure of approximately 24 kPa, the specific surface area decreases rapidly as the residual carbonate increases slightly. Conversely, when a value of the residual carbonate of about 10 weight-% is reached, the specific surface area starts to increase again slowly as higher partial pressures of
carbon dioxide are used. Simultaneously, the residual carbonate increases rapidly up to equilibrium, as already shown in Figure 3. Moreover, it is evident that the specific surface area decreases with increasing time, which can be seen in Figure 4.

![Graph showing the relationship between residual carbonate and specific surface area.](image)

**Fig. 4** Lime mud I. Balls. Symbols as in Figure 3.

The size of the balls seems very much dependent upon the residual carbonate. An almost linear relationship can be seen in Figure 5, with decreasing ball diameters as the residual carbonate increases. For low partial pressures of carbon dioxide in the sintering atmosphere, the results indicate that the size of the balls seems to increase with time. When equilibrium is reached, time does not seem to be as important to the size any more.

It is obvious that the size of the balls has a significant effect on their strength. In Figure 6 it can be seen how, at constant time and increasing partial pressure of carbon dioxide, the strength increases and the balls decrease in size. At equilibrium and higher partial pressures of carbon dioxide, the strength increases with increasing time, even though the size of the balls is almost constant. In Figure 7 it is evident that at constant time, as the residual carbonate increases with increasing carbon dioxide, so does the strength. The strength of the balls is plotted versus the specific surface area in Figure 8. It can be seen that with increasing time, the strength increases and the specific surface area decreases at constant, relatively high, concentrations of carbon dioxide. The increase in strength becomes more rapid, and the decrease in specific surface area slower at higher concentrations of carbon dioxide (the lines in the graph are there to make it easier to follow the trend described). The strength after five hours with a partial pressure of carbon dioxide of 36 kPa is high. When all kinds of comparisons were made, it was observed that this particular experiment gave unusually small balls, which results in a higher strength than could be expected.

In the second part of the study, the influence of temperature was investigated, whereby lime mud II was used. Figure 9 shows how equilibrium is reached for two different temperatures. At a partial pressure of carbon dioxide of 90 kPa, the samples at 750°C reached a high level of carbonate and, at 850°C,
the same level is reached at about 60 kPa. At 900°C, equilibrium is never reached.

The second lime mud was observed as having a different relationship between specific surface area and residual carbonate compared with the first lime mud (fig. 4), Figure 10. Here, it can be seen how the surface area decreases with increasing residual carbonate over the whole range at both 750 and 850°C. It may seem as though the reduction of the specific surface area ceases when equilibrium is reached. The results shown in Figure 10 represent powder, since not enough balls were created with the second lime mud. The few balls that were formed were not hard enough to withstand strength measurements, which is the reason why no comparisons in strength for the different temperatures could be made.

Discussion

It is shown that with the equipment used, the calcination reaction at partial pressures of carbon dioxide below equilibrium takes almost seven hours to be completed, but the residual carbonate value after five hours is close to the seven-hour value. After only 1
The first one showed a minimum in specific surface varying the partial pressure of carbon dioxide and the balls still have a high residual carbonate, probably as a result of a poor heat transfer rate. The equilibrium partial pressure of carbon dioxide, calculated using the expression of Baker (1962), agrees well with the measured data where, when using this partial pressure, it can be seen how the same high value of residual carbonate is obtained after both five and seven hours.

The behaviour of the specific surface area when varying the partial pressure of carbon dioxide and thus the residual carbonate is ambiguous, as the two different lime muds show different trends at 850°C. The first one showed a minimum in specific surface area at about 10 weight-% of residual carbonate. It looked as if calcium carbonate, with its larger particles, sinters more slowly compared with calcium oxide exposed to carbon dioxide. The second lime mud, on the other hand, decreases its specific surface area with increasing residual carbonate over the whole range investigated. This can be observed at both 750 and 850°C, and is in accordance with the findings of Lindblom et al. (1996), when the influence of carbon dioxide on the sintering of reburned lime mud in a tube reactor was studied. This equipment allowed a small amount of lime mud, placed on a porous quartz glass disc, to be penetrated by gas. The reduction in specific surface area with increasing carbon dioxide is thought to be caused by higher mobility in the solid when the reacting gas is present. It seems as though the reduction of the surface area finally slows down significantly. The particles involved have become large by then, and the sintering process is consequently slow.

The same trend as was seen for the two lower temperatures with decreasing surface areas with increasing residual carbonate could not be seen at 950°C, where the residual carbonate is low, independent of carbon dioxide. The specific surface area is higher at 950°C and low residual carbonate than for the samples with high residual carbonate at 850°C. A possible explanation could be that mobility is not as high for the first condition as the latter, since the calcination reaction is strongly favoured when compared to recarbonation at this high temperature. Tran et al. (1992) observed the same behaviour when they sintered formed pellets. They report that sintering at a high temperature without recarbonation gave a much lower strength than sintering at a low temperature with recarbonation.

There are substantial differences in the compositions of the two lime muds used in the present study. The first one has less calcium carbonate and significant amounts of sodium and phosphorus, but SEM images did not reveal any major differences in microstructure between them. The second one resembles the one used in the earlier study with the tube reactor; maybe that is why their behaviours can be compared. Furthermore, when using the first one, balls were formed under most of the conditions investigated, which was not the case for the second one. It may be that the first lime mud, because of some kind of surface phenomenon due to substantial concentrations of sodium and phosphorus, forms balls and rings more easily. Thus, the following discussion regarding balls is based on the results from lime mud I only. It should be noted that the results suggest that the balls are formed at an early stage, before calcination.

For partial pressures of carbon dioxide below equilibrium, the size of the balls increases with time. It is evident that, at those conditions, the lime keeps adhering to balls already formed, which makes them grow. When equilibrium is reached, neither the residual carbonate nor the ball size are affected by time after five hours, as the same values are obtained after seven hours. Calcium oxide seems more prone to form large balls than calcium carbonate.

The relation between ball size and its strength shows a decrease in strength with an increase in diameter. The same observation was made in a previous study (Lindblom and Theliander 1998), where the strength of several industrial reburned limes were tested, and balls of different sizes were used. The smaller balls have most likely been allowed to sinter more, because of homogeneous heating. It should be mentioned that the strength measurements give a high average error, about 50%. Considering the various ball sizes present after an experiment, and how they are picked manually for strength measurements, the high average error seems reasonable. All trends discussed here can, despite the high average error, still be discerned.

The strength was also shown to increase with increasing residual carbonate. Both Skrifvars et al. (1992) and Tran et al. (1992) formed pellets that were sintered under controlled conditions, and they both observed the same behaviour. According to Skrifvars et al. (1992), the greatest strength development occurs just before decomposition. Tran et al. (1992) claims a linear relationship between strength and degree of recarbonation. It is believed that the way in which the solid material closes its pores when it recarbonates accounts for the increased strength.

The strength of the balls, at constant partial pres-
sure of carbon dioxide and temperature, increases with time as the specific surface area decreases. The reduction in specific surface area with increasing time is in accordance with several earlier studies (Hanson 1993, Lindblom et al. 1996). The simultaneous increase in strength is probably due to the reduction in porosity as sintering proceeds. The exact same behaviour was identified in the study concerning the sintering of formed lime pellets (Lindblom and Theliander 1998).

When studying Figure 8 it is obvious that, for higher partial pressures of carbon dioxide, the reduction of surface area slows down at the same time as the increase in strength accelerates. Different kinds of mechanisms seem to be involved during the sintering process, depending on the partial pressure of carbon dioxide. The results at low partial pressures with a rapid reduction in surface area, but not very strong agglomerates, could suggest that small particles have become large, but that the bonds between them are not very strong. Some kind of bulk diffusion process could be expected to make the particles grow in such a manner. Conversely, at higher partial pressures, a surface diffusion process may result in strong necks between particles without the same densification as at lower partial pressures. The high partial pressures, of course, result in extensive recarbonation, and this would make a surface diffusion process likely to occur.

The fact that strength increases with increasing residual carbonate means that, in an industrial rotary kiln, whenever the calcined material recarbonates, the strength is enhanced. Recarbonation occurs when either the temperature is low enough and/or the concentration of carbon dioxide is high enough. The conditions in the middle of the kiln, close to the beginning of the calcining zone, enhance recarbonation and, not surprisingly, severe ring problems are common in this region. In this area, even a small drop in temperature may lead to recarbonation.

Balls were used in the present study in order to measure agglomerate growth and strength. The results obtained could be used to explain ring growth and hardening in industrial rotary kilns. They show that, besides the fact that rings are able to grow with increasing time if the solid material is influenced by some kind of as yet unknown surface phenomenon, they will also become harder whenever recarbonation occurs. The combination of growing rings which become harder with time makes the middle of the industrial rotary kiln prone to severe ring formation.

Concluding remarks

The balls were found to behave slightly differently compared with the rings and dusts in that they generally had a larger specific surface area and a higher content of carbonate. This is thought to be due to a lower heat transfer rate. It was shown that, at 850°C, the degree of calcination is high at partial pressures of carbon dioxide up to 24 kPa in the sintering atmosphere. At higher partial pressures, the residual carbonate increases rapidly and, at as high partial pressures as 60 kPa, equilibrium is obtained.

The two lime muds showed different behaviours in terms of the influence of carbon dioxide on sintering. The first one reached a minimum in specific surface area at about 10 weight-% of residual carbonate, while for the second one, the specific surface area decreased with increasing residual carbonate over the whole range investigated. For the second lime mud, at the highest temperature used, i.e. 950°C, the residual carbonate was low at all partial pressures of carbon dioxide. For these samples, the specific surface area was higher than for those with a high residual carbonate at 850°C.

The strength of the balls decreases as they increased in size and, furthermore, the strength increased with increasing residual carbonate. At constant temperature and partial pressures of carbon dioxide, the strength of the balls increased with time and the specific surface area decreased. Also, as the partial pressure of carbon dioxide increased, the reduction of the specific surface area became slower and the increase in strength more rapid.

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References


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