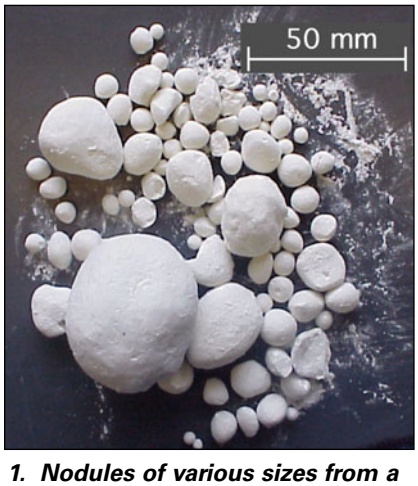
Correlation between nodule size and residual carbonate content in lime kilns

HONGHI TRAN, SHAWN VOLLICKS, MIKE GAUTHIER, AND CHARLIE MCNEIL

ABSTRACT: Field studies were performed on several lime kilns to establish a correlation between the size of reburned lime nodules and their residual carbonate content. Nodules with a diameter smaller than 20–30 mm have a low, uniformly distributed residual carbonate content. Larger nodules have an uncalcined core and thus contain significantly more residual carbonate. Mills that test only small nodules for residual carbonate may have much lime mud dead load unknowingly circulating in the lime cycle.

Application: Kraft mills should develop a better procedure for determining residual $CaCO_3$ content in the product lime. The procedure should include testing of large nodules.

In lime kiln operation, reburned lime typically forms nodules (round pellets) ranging in diameter from 5–50 mm (**Fig. 1**). At one extreme, the reburned lime forms powdery, fine pellets similar to the dried mud from which it originates; at the other extreme, the reburned lime forms balls with a diameter >100 mm. Size is an important determinant in lime quality and kiln throughput. Small nodules may lead to particle entrainment and dust recirculation. Large nodules may have insufficient residence time in the kiln to fully calcine, causing more residual carbonate that makes slaking and causticizing processes less efficient.



1. Nodules of various sizes from a lime kiln.

The formation process for lime nodules, the kiln operating parameters that affect nodule formation, and the optimum size of nodules are not well understood. The consensus is that nodules form as a result of agglomeration and consolidation caused by the rotating, tumbling, and sliding motions of the bed material as it moves through the kiln. The solids and sodium contents of the feed mud, the feed end and front end temperatures of the kiln, and the retention time of the bed material in the kiln are believed also to affect nodule formation.

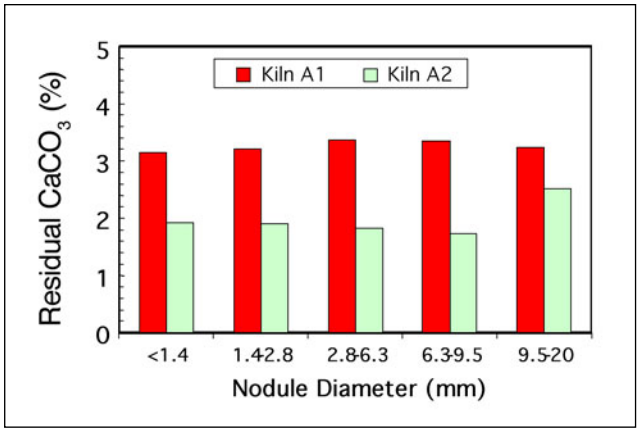
This work is part of a comprehensive research program at the University of Toronto to investigate the cause and effect of various issues in lime kiln operation. Laboratory studies were done to examine the mechanisms of nodule formation and factors affecting the formation. Field studies were performed on lime kilns at several kraft pulp mills to examine optimum size ranges for lime nodules. Results of the field studies and their practical implications are presented. Results of the laboratory studies will be summarized in another paper.

METHODS AND MATERIALS

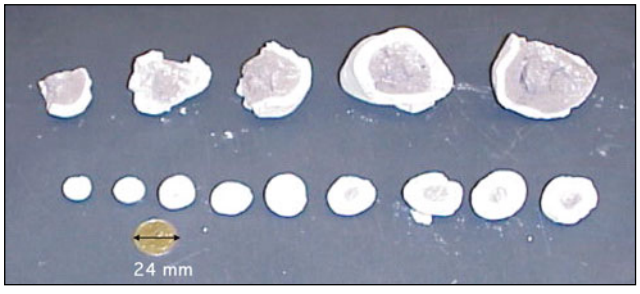
Mill A studies

Mill A has two identical Allis-Chalmers lime kilns (Kiln A1 and Kiln A2). The kilns were started up in 1965 and 1983, respectively. Each has a product cooler, a 3.05-m inside diameter (ID), a 76-m length, and production capacity of 200 tons/day of CaO. Kiln A1 is usually fired with natural gas plus noncondensible gass (NCG) and stripper off gas (SOG). Kiln A2 is usually fired with natural gas and tall oil. Occasionally, the burning practice is reversed.

From each kiln, two sets of product lime samples were collected using a steel pail attached to the end of a long rod. The sampling pail was inserted through an access door on the firing hood of each kiln to collect the nodules before they entered the satellite coolers. The nodules were sieved into different size ranges, which were analyzed for residual $CaCO_3$ using a reburned lime analyzer at the mill. **Figure 2** shows the residual $CaCO_3$ in nodules of different sizes collected from Kiln A1 and Kiln A2 on the same day. Up to a diameter of 20 mm, there was no significant difference in residual $CaCO_3$. The residual $CaCO_3$ in Kiln A1 samples was about 3.2 wt%, slightly higher than that for Kiln A2, presumably a result of the lower front end temperature in Kiln A1 at the time of sampling. These small nodules (<20 mm) were white or pale yellow and had a relatively uniform cross section. They did not have a dark spot (or core) at the center.



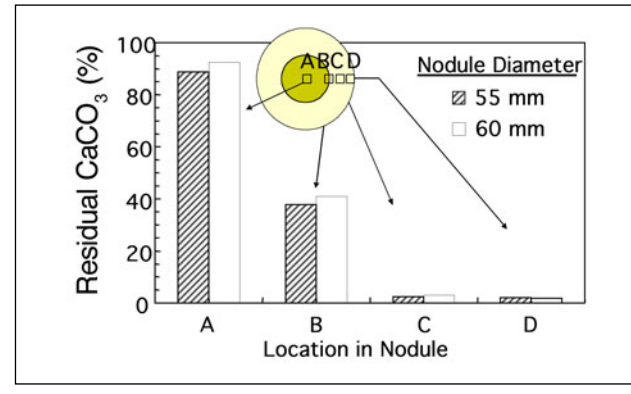
2. Residual $CaCO_3$ content in nodules of various size ranges collected from Kiln A1 and Kiln A2.



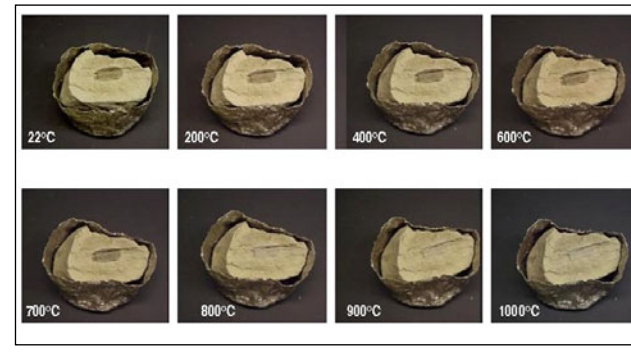
3. Cross section of nodules from Kiln A2. Nodules larger than about 25 mm have a dark grey core surrounded by a white shell.



4. Cross section of a 60-mm lime nodule from Kiln A1.



5. Residual $CaCO_3$ content at different locations in two large lime nodules from Kiln A2.



6. Effect of heat treatment on core color.

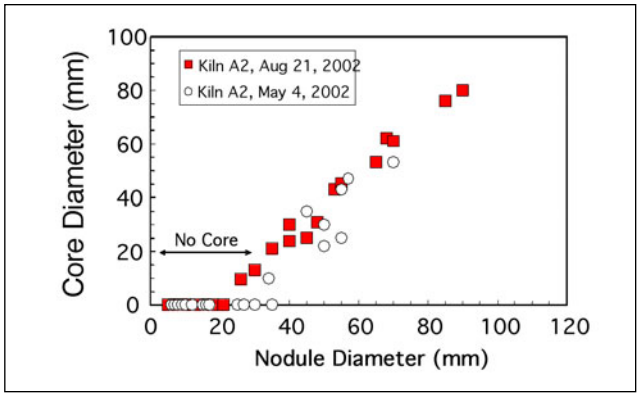
Nodules larger than the size of a quarter (>24 mm), however, had a darker core at the center surrounded by a whiter shell (**Fig. 3**).The thickness of the white shell was relatively constant, regardless of the nodule size, while the size of the dark core increased with increasing nodule size.The left side of Fig. 4 shows the cross section of a 60-mm diameter nodule containing a dark core.The core was much softer than the shell and could easily be scooped out, as shown on the right of **Fig. 4**.

The residual $CaCO_3$ content of two large nodules (55 mm and 60 mm) at different locations within the nodules was determined using a thermo gravimetric analyzer. As shown in **Fig. 5**, for both nodules, the dark core (location A) contained about 90 wt% $CaCO_3$; the boundary (location B) had about 40 wt% $CaCO_3$; and the white shell (locations C and D) contained about 3 wt% $CaCO_3$. These findings suggest the dark core is essentially uncalcined lime mud and the shell is calcined lime or lime mud that has already been calcined.

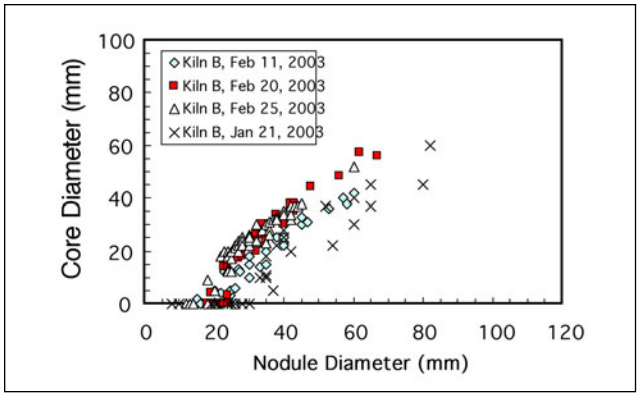
Laboratory tests were done to verify the findings. In each test, a lime nodule with an average diameter of 40–50 mm was broken into two pieces to expose its core. One piece was placed in a platinum crucible and heated in a muffle furnace. After heating at a set temperature for 10 min., the crucible was removed from the furnace, visually examined, photographed, and then returned to the furnace for another 10-min. heat treatment at a higher temperature. The heat treatment was repeated at 100°C increments until the temperature reached 1000°C.

Figure 6 shows that the dark appearance of the core remained unchanged until the temperature exceeded 800°C, the expected calcination temperature of the mud. The dark color of the core resembled the color of lime mud, while the bright color of the shell resembled the color of calcined lime collected from the same kiln. Similar results were obtained for all tests. The disappearance of the dark core in the large nodules after they were heated at temperatures > 800°C implies that the core temperature must have been <800°C in the kiln.

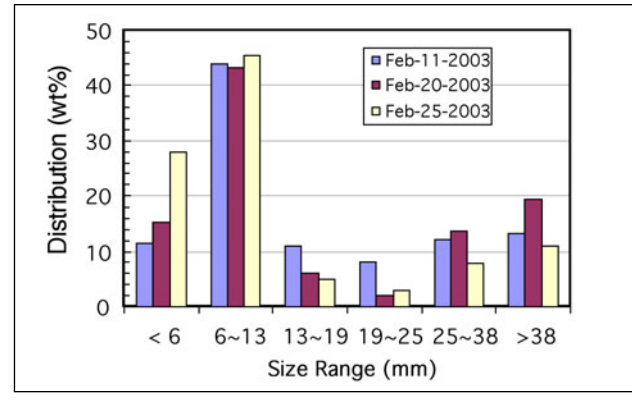
Figure 7 shows relationships between the average



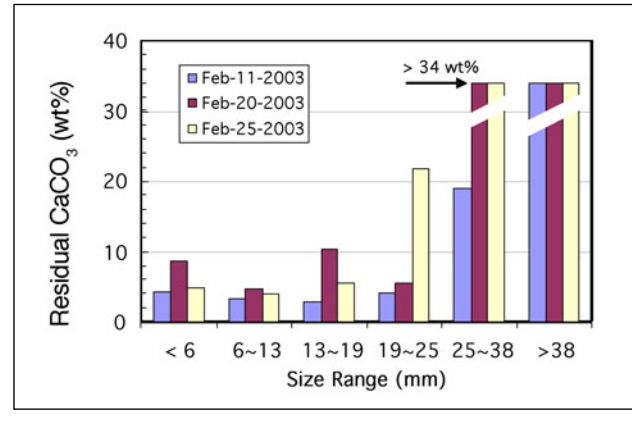
7. Relationship between core diameter and nodule diameter in Kiln A2.



8. Relationship between core diameter and nodule diameter in Kiln B.



9. Size distribution of nodules from Kiln B.



10. Residual carbonate in various sized nodules from Kiln B. Five samples had residual carbonate content higher than 34 wt%, the upper limit of the residual $CaCO_3$ analysis used in this study.

core size and average nodule size for two sets of nodules collected from Kiln A2 on different days. The results clearly show that small nodules (<20–30 mm in diameter) have no core, whereas larger nodules have a core size proportional to the nodule diameter.

Mill B studies

The lime kiln at Mill B (Kiln B) is a 1989 F.L. Smidth unit with a designed production capacity of 350 tons/day of CaO. The kiln has a 3.5-m ID, 101-m length, and 9-tube product coolers. The kiln burns natural gas together with concentrated noncondensible gas (CNCG) and SOG. Four sets of nodule samples were collected on different days. The correlation between core size and nodule size for each set was examined, as was the effect of nodule size on the residual carbonate content.

Figure 8 shows core size versus nodule size for the four sets of Kiln B samples. Nodules with a diameter <20 mm had no core, while nodules >25 mm had a core diameter that linearly increased with the nodule diameter. The core size appears to increase suddenly, from 0 (no core) to about 15 mm, as the nodule size approaches 20 mm to 30 mm. These results are consistent with those from Kiln A2 (Fig. 7).

The size distribution of the nodule samples collected on three different days in February 2003 was determined by sieving the samples into six different size fractions using five sieve sizes: <6 mm (0.25 in.); 6–13 mm (0.5 in.); 13–19 mm (0.75 in.); 19–25 mm (1 in.); 25–38 mm (1.5 in.); and >38 mm. Also, the weight of the material remaining in each sieve size was measured. As shown in **Fig. 9**, all three sets of nodules have a similar size distribution, although the February 11, 2003 samples contained slightly more small nodules than the other two samples. The 6–13 mm (0.25–0.5 in.) size range is the most predominant, accounting for about 45% of the total sample on a weight basis. Nodules >25 mm (1 in.) account for 20%–35% of the sample.

A standard reburned lime analyzer was used to determine the residual carbonate content of each size range. The procedure involved titrating pulverized lime samples with HCl, measuring the amount of CO_2 released, and estimating the residual carbonate. The results are shown in **Fig. 10**. Nodules <19 mm contained an average 5 wt% $CaCO_3$, while those >25 mm had

a much higher $CaCO_3$ content. Five samples had a $CaCO_3$ content higher than 34 wt%, the upper limit of the residual $CaCO_3$ content that can be analyzed at the mill.

Table I summarizes the major operating conditions of Kiln B during the tests. The front end kiln temperature was somewhat lower during the February 11, 2003, test than during the tests on February 20 and 25, 2003. This finding reflects the lower fuel-to-mud ratio at which the kiln was operating on February 11, 2003. The lower front end temperature is not consistent with the sample's lower residual $CaCO_3$ content found that day (Fig. 10). The results imply that nodule size and distribution may affect the residual $CaCO_3$ content of the product lime.

	February 11, 2003 06:00-10:00	February 20, 2003 7:30-11:30	February 25, 2003 6:48-10:24
Lime production (tons/day CaO)	358	351	353
Kiln rotational speed (rpm)	1.65	1.65	1.65
Mud feed (L/s)	24.5	24.0	23.5
Gas flow rate (SCM/H)	2097	2106	2182
Fan-op (%)	78.2	72.3	76.9
Draft (mm H_2O)	-53.9	-53.2	-50
Feed end temp (°C)	301	301	307
Front end temp (°C)	1106	1159	1130

I. Major operating conditions of Kiln B during the tests.

STUDIES AT OTHER MILLS

Studies were performed on several conventional kilns and kilns equipped an external lime mud drier (LMD) at other pulp mills. In all cases, the results obtained were similar; that is, nodules with diameters smaller than about 20–25 mm had no core, while larger nodules had core size that increases with the nodule size.



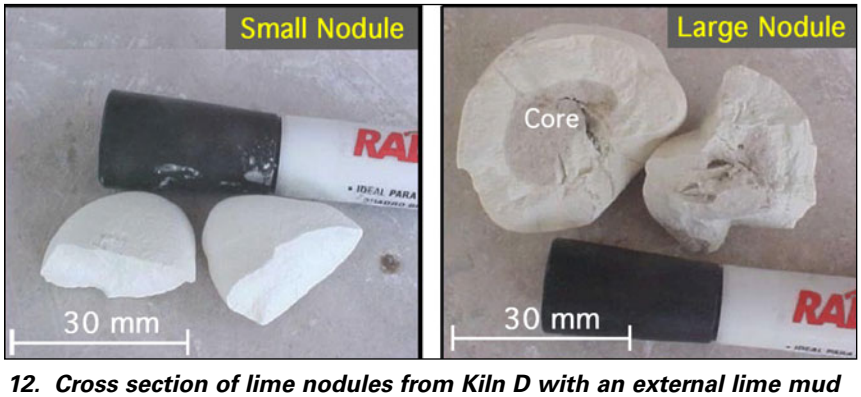
11. Lime nodules from Kiln C with an external lime mud drier.

Kilns equipped with an LMD usually have no chain section. Wet lime mud is flashed with flue gases at the kiln feed end and dried. The dried mud particles are collected in a cyclone separator or an electrostatic precipitator or both before being fed back into the kiln. The mud material is usually dried and has fewer tendencies to stick on the kiln wall than in kilns without an LMD. Nodules in kilns with an LMD are usually smaller and more uniform than those in kilns without an LMD (**Fig. 11**) but larger nodules also have cores (**Fig. 12**).

DISCUSSION

Core size vs. nodule size

The results clearly suggest that the size of the uncalcined core in a reburned lime nodule shows a strong correlation with the size of the nodule. Nodules with diameter <20 mm do not usually have cores but nodules >25 mm have cores with diameters that increase linearly with the nodule diameter. The correlation between core size and nodule size was further examined by performing linear regressions on individual data sets collected from Kiln A2 and Kiln B for nodules >25 mm.



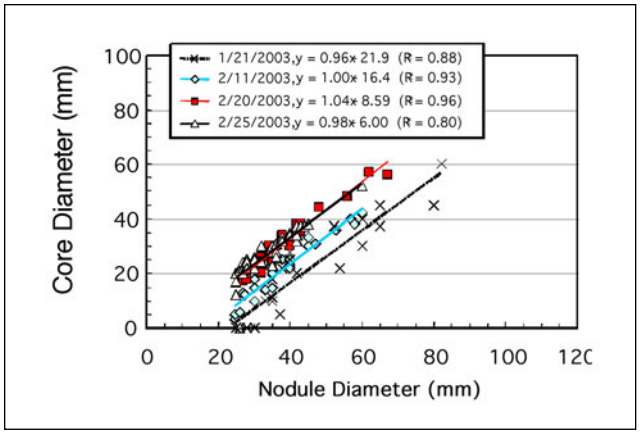
12. Cross section of lime nodules from Kiln D with an external lime mud drier.

Figure 13 shows the trend lines and linear regression equations determined by Microsoft Excel for Kiln B data. The lines appear to be parallel with a slope of about 1.0. The R^2 values of the lines are all greater than 0.8, indicating a good linear correlation between core size and nodule size.

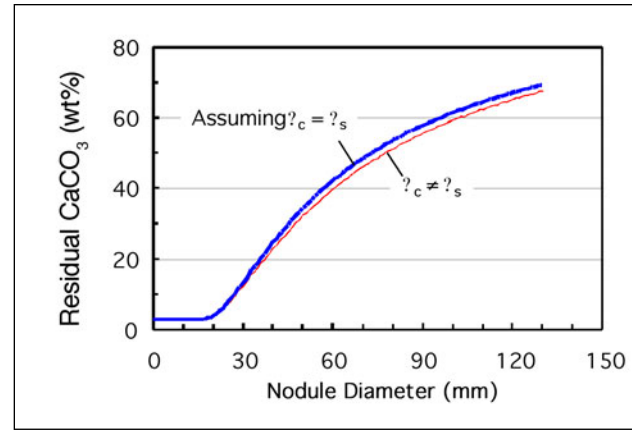
Similar results were also obtained for nodule samples collected from Kiln A2 (Fig. 7). In this case, the linear regression equations and R^2 values were, respectively, $y = 1.18x - 28.2$ and $R^2 = 0.89$ for the May 4, 2002, samples and $y = 1.07x - 17.2$ and $R^2 = 0.96$ for the August 24, 2002, samples.

Using the averaged values of all linear regression equations obtained for Kiln A2 and Kiln B, the relationship between the core diameter (D_C) and nodule diameter (D_N), expressed in mm, may be approximated as follows (Eq. 1 and 2):

$$\text{For } D_N < 25\,\text{mm} \qquad D_C = 0 \qquad (1)$$



13. Trend lines and linear regression equations for Kiln B data.



14. Relationships between residual $CaCO_3$ content and nodule diameter. Thin curve calculated using Eq. 1, 2, 5, and 6. Thick curve calculated using Eq. 1, 2, and 8.

$$\text{For } D_N \geq 25\text{mm} \qquad D_C = 1.04\, D_N - 16.4 \tag{2}$$

Residual $CaCO_3$ content vs. nodule size

As shown in Fig. 5, a large nodule comprises two parts: a core and its surrounding shell. The core is essentially lime mud that has not been calcined and typically has a $CaCO_3$ content of about 90 wt%. The shell is calcined lime, which typically contains about 3 wt% residual $CaCO_3$. The presence of the lime mud core would undoubtedly increase the overall $CaCO_3$ content of the lime nodule.

Using Eq. 1 and 2, and assuming that nodules are spherical, it is possible to derive Eq. 3 and 4 for estimating the overall residual $CaCO_3$ content of a lime nodule (R_N), as a function nodule diameter:

$$\rho_N = (\rho_C - \rho_S)\left(\frac{D_C}{D_N}\right)^3 + \rho_S \tag{3}$$

$$R_N = \left(R_C\frac{\rho_C}{\rho_N} - R_S\frac{\rho_S}{\rho_N}\right)\left(\frac{D_C}{D_N}\right)^3 + R_S\frac{\rho_S}{\rho_N} \tag{4}$$

where ρ_N, ρ_C and ρ_S are the densities of nodule, core, and shell; R_N, R_C, and R_S are the % residual $CaCO_3$ content of nodule, core, and shell; and D_N and D_C are the diameters of nodule and core.

The properties of core and shell, respectively, are the same as the properties of lime mud and calcined lime. In this study, ρ_C = 0.92 g/cm³, ρ_S = 1.03 g/cm³, R_C = 90%, and R_S = 3%. Using these values, Eq. 3 and 4 become Eq. 5 and 6:

$$\rho_N = -0.11 \times \left(\frac{D_C}{D_N}\right)^3 + 1.03 \tag{5}$$

$$R_N = \left(\frac{79.7}{\rho_N}\right)\left(\frac{D_C}{D_N}\right)^3 + \frac{3.09}{\rho_N} \tag{6}$$

If ρ_C and ρ_S are both taken as being approximately 1.0 g/cm³, then from Eq. 3, ρ_N is approximately equal to ρ_C and ρ_S. Thus, Eq. 4 can be further simplified as follows (Eq. 7):

$$R_N = (R_C - R_S)\left(\frac{D_C}{D_N}\right)^3 + R_S \tag{7}$$

For R_C = 90% and R_S = 3%, Eq. 7 becomes:

$$R_N = 87 \times \left(\frac{D_C}{D_N}\right)^3 + 3 \tag{8}$$

Figure 14 plots the residual $CaCO_3$ content as a function of nodule diameter. The thick curve was based on Eq. 1, 2, 5, and 6 without assuming $\rho_C = \rho_S$. The thin curve was based on Eq. 1, 2, and 9, which assumes $\rho_C = \rho_S$. Only a small discrepancy between these curves is observed, which suggests that the simplified Eq. 8 is reliable. The calculations confirm the significant effect of nodule size on the overall residual $CaCO_3$ content.

At a pulp mill, it may be advisable to first establish the correlation between D_C (core diameter) and D_N (nodule diameter) and the R_C and R_S values, which are the same as the typical $CaCO_3$ content of lime mud and lime at the mill. Then, the Eq. 1, 2, and 8 that are specific to the mill can be determined. Once established, the equations can be used to calculate residual $CaCO_3$ content of a lime nodule based only on its diameter.

PRACTICAL SIGNIFICANCE

In normal mill practice, residual $CaCO_3$ content is determined every 4 to 8 hours, usually on lime nodules typically sized 10–30 mm; large nodules are seldom tested. Such a practice may lead to erroneous measurement of residual $CaCO_3$ content. As suggested in Fig. 14, the actual value could be significantly higher if the reburned lime contains many large nodules. Such a situation could have an adverse impact on the causticizing plant operations.

The size distribution of nodules in lime kilns is usually unknown. However, Fig. 10 indicates that, in a particular kiln, 75% of the product lime consists of nodules <25 mm and 25% of nodules >25 mm. If the average diameter of large nodules is assumed to be 50 mm, then their average residual $CaCO_3$ would be about 35 wt%, according to Fig. 14 (thick curve). Therefore, overall residual $CaCO_3$ would be (0.75 x 3%) + (0.25 x 35%) = 11%. This value is 8% higher than the value that would have been obtained by testing only small nodules.

In mills that only test small nodules, it is likely that much carbonate dead load is circulating within the lime cycle, which burdens the causticizing equipment and lime kiln. Therefore, it is important for mills to develop or adopt an improved procedure for determining the residual $CaCO_3$ content in the product lime which must include large nodules. One example is to analyze lime samples after the lime crusher, not before. However, depending on the amount of oversize nodules that come out of the kiln, the residual $CaCO_3$ target may have to be raised to avoid overcooking the smaller nodules.

Because it is not known how nodules form and grow in the kiln, it is difficult to devise a kiln operating strategy that avoids formation of large nodules with uncooked cores and produces small nodules with low, uniform carbonate content. Nodules larger than 80 mm (about 3 in.) contain more than 50 wt% $CaCO_3$. Dead load in the causticizing plant could be reduced by screening large nodules out of the product lime, crushing them, and returning them to the kiln.

SUMMARY

Field studies were performed on several lime kilns to establish a correlation between the size of returned lime nodules and their residual carbonate content. The results show that:

•Nodules <20–30 mm in diameter have low, uniformly distributed residual carbonate content.

•Nodules larger than this critical size have an uncalcined core and thus contain significantly more residual carbonate. The core diameter (D_C, mm), and the residual $CaCO_3$ content (R_N, %) may be approximated as a function of nodule diameter (D_N, mm)

INSIGHTS FROM THE AUTHORS

In lime kiln operation, reburned lime typically forms nodules with diameters ranging from 5–50 mm. Size influences lime quality and the kiln throughput. Small nodules may lead to particle entrainment and dust recirculation. Large nodules may not have sufficient residence time in the kiln to fully calcine; they contain more residual carbonate, which reduces the efficiency of slaking and causticizing processes.



Tran



Vollicks



Gauthier



McNeil

Field studies established a correlation between the size of reburned lime nodules and their residual carbonate content. Nodules <20–30 mm in diameter have low, uniformly distributed residual carbonate content. Larger nodules have an uncalcined core and contain significantly more residual carbonate. Mills that only test small nodules for residual carbonate probably have much lime mud dead load circulating in the lime cycle, which burdens the causticizing equipment and lime kiln.

Nodules larger than 80 mm (about 3 in.) contain more than 50 wt% $CaCO_3$. Mills could reduce the dead load in the causticizing plant by screening large nodules out of the product lime, crushing them, and returning them to the kiln.

Tran is professor and director at the University of Toronto Pulp and Paper Centre, Toronto, Ontario, Canada. Vollicks is with Domtar Inc., Espanola, Ontario, Canada. Gauthier and McNeil are with DMI-Peace River Pulp, Peace River, Alberta, Canada. Email Tran at tranhn@chem-eng.toronto.edu.

using the following equations:

$$D_C = 1.04\, D_N - 16.4$$

$$R_N = 87 \times \left(\frac{D_C}{D_N}\right)^3 + 3$$

•For more accurate estimations, individual mills may need to first establish the correlation between D_C and D_N, the R_C and R_S values which are equal to the typical $CaCO_3$ contents of lime mud and lime, and then determine equations that are specific to the mill.

•In mills where only small nodules are tested for residual carbonate, it is likely that much lime mud dead load is circulating in the lime cycle, which burdens the causticizing equipment and lime kiln. **TJ**

ACKNOWLEDGMENTS

This work was part of the research program on increasing throughput and reliability of recovery boilers and lime kilns. The program is supported by Alstom Power Inc., Andritz Corp., Aracruz Celulose S.A., Babcock & Wilcox Co., Boise Cascade Corp., Bowater Canada Inc., Canadian Forest Products Ltd., Clyde-Bergemann Inc., DMI Peace River Pulp, Domtar Inc., Georgia-Pacific Corp., International Paper Co., Irving Pulp & Paper Ltd., Kværner Pulping Technologies, MeadWestvaco Corp., Stora Enso Research, Votorantim Celulose e Papel, and Weyerhaeuser Paper Co. Support also comes from the Natural Sciences and Engineering Research Council of Canada (NSERC) through its Collaborative R&D Program.

Submitted: November 29, 2005
Revised: August 23, 2006
Accepted: August 23, 2006

This paper is also published on **www.tappi.org** and summarized in the April issue of Paper360° magazine.

AWARD WINNER ANNOUNCED



Douglas W. Reeve, Professor in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto received PAPTAC's John S. Bates Memorial Gold Medal. The award was presented to Reeve at PAPTAC's 93rd Annual Meeting in February, for his long-term contributions to the science and technology of the pulp and paper industry.

Reeve was the founding Director of the University of Toronto Pulp & Paper Centre, and served to 2001. He is recognized as a leader of the pulp and paper industry courses and conferences. Reeve joined the Technical Section, CPPA, now PAPTAC, in 1968.

He has been a TAPPI member since 1971. Reeve founded and chaired the Bleach Plant Operation seminars, the Kraft Recovery Operations seminar and the International Chemical Recovery conference. He received the 1987 Pulp Manufacture Award and Johan C.F.C. Richter Prize for his outstanding contributions in this division. He was named a TAPPI Fellow in 1988. Reeve also served on TAPPI's Board of Directors from 2000-2002.