

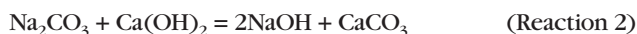
# Measurement of free lime content in lime mud

XIAOSONG MAO, WEI REN, AND HONGHI TRAN

**ABSTRACT:** Overliming and the consequent presence of unreacted lime (or free lime) in the lime mud are commonly believed to be the cause of many problems in the operation of causticizing plants and lime kilns in kraft pulp mills. The free lime content in lime mud is typically determined in mill laboratories using a so-called ammonium chloride ( $\text{NH}_4\text{Cl}$ ) method and in commercial laboratories using a thermal decomposition (TD) method. Over the years, we analyzed many lime mud samples from mills and found that the free lime content was consistently low, < 3 wt% calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), even in cases where overliming was suspected to have caused problems. A systematic study was therefore conducted to investigate the validity of free-lime measurement methods, the reason for the consistently low free lime content in lime mud, and if free lime values can be used to indicate overliming. The results show that the  $\text{NH}_4\text{Cl}$  method is not suitable for determining free lime. The TD method is good, but the possible interference of magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) must be taken into account. Since most pulp mills perform their free lime analysis on mud samples collected from pre-coat filters which have been washed, the resulting free lime value is low, and thus, cannot be used to assess the extent of overliming in the causticizing plant.

**Application:** Mills should be aware that the conventional  $\text{NH}_4\text{Cl}$  method for measuring the free lime content in lime mud does not work. It gives a free lime value that is low and cannot be used to assess the extent of overliming in the causticizing plant.

In the causticizing plant of kraft pulp mills, lime ( $\text{CaO}$ ) is used to convert sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in green liquor into sodium hydroxide ( $\text{NaOH}$ ), one of the two main chemicals used in the pulping process [1,2]. The causticizing process involves two main reactions:



The slaking reaction (Reaction 1) is fast and occurs in the slaker to form calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ). The causticizing reaction (Reaction 2) is much slower, starting in the slaker after  $\text{Ca}(\text{OH})_2$  has been formed and continuing to occur in the causticizers that follow the slaker. These reactions convert the green liquor to white liquor, and in the process, produce calcium carbonate ( $\text{CaCO}_3$ ), which, together with small amounts of unreacted  $\text{Ca}(\text{OH})_2$  and other insoluble impurities, forms a solid mass known as lime mud. Lime mud is separated from the white liquor in a clarifier or a pressurized filter. The clarified or filtered mud is washed to remove the white liquor residue and dewatered on a pre-coat drum filter before being fed into a lime kiln where it is converted back into  $\text{CaO}$ .

The causticizing reaction is an equilibrium reaction. This means that under a given operating condition, the reaction proceeds only when the  $\text{NaOH}$  concentration (more precisely, the  $\text{OH}^-$  concentration) in the liquor is below the equilibrium

concentration of the system [3-6]. Above this equilibrium concentration, which is determined by thermodynamics, the reaction reverses, producing  $\text{Ca}(\text{OH})_2$  and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or carbonate ion ( $\text{CO}_3^{2-}$ ) until a new equilibrium is reached. The degree to which the causticizing reaction proceeds is known as causticizing efficiency, which is defined as in Eq. (1):

$$\text{CE} = \frac{[\text{OH}^-]}{[\text{OH}^-] + [\text{CO}_3^{2-}]} \times 100 \quad (1)$$

where CE is causticizing efficiency in %;  $[\text{OH}^-]$  and  $[\text{CO}_3^{2-}]$  are respectively concentrations of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  in the liquor, expressed as g/L  $\text{Na}_2\text{O}$ . Since the liquor CE is linearly proportional to the  $\text{OH}^-$  concentration (Eq. [1]), many mills use CE to indicate the magnitude of  $\text{OH}^-$  concentration, while considering the equilibrium CE as the maximum attainable  $\text{OH}^-$  concentration in the liquor.

Equilibrium, CE, is a strong function of the total titratable alkali (TTA) and sulfidity of the liquor [1,2,6]. In theory, it is equivalent to the maximum liming ratio (or  $\text{CaO}/\text{Na}_2\text{CO}_3$  molar ratio) that the system can handle. For example, under a causticizing condition where the equilibrium CE is 88%, the amount of lime added to the system must be such that the liming ratio is below or equal to 0.88. Exceeding this equilibrium value will cause the system to be “overlimed” and the resulting lime mud to contain unreacted  $\text{Ca}(\text{OH})_2$  or “free

# LIME MUD

lime". In practice, in order to avoid overliming, many mills simply set their CE target at about 5% below the equilibrium CE value [7].

Since the causticizing reaction takes time to reach equilibrium, a substantial amount of free lime may still be present in the lime mud, even when the lime dosage is lower than that theoretically required by the reaction. Furthermore, in cases where the lime reactivity is low and the residence time for the causticizing reaction is short, mills often unknowingly add more lime than they need to in order to achieve their desired CE target. This would lead eventually to an overliming condition and a high free lime content in lime mud.

Overliming and free lime are commonly believed to cause many problems in the causticizing plant and lime kiln operations. The problems include poor mud settling, "dirty" white liquor, filter cloth clogging, low mud solids, and high sodium content in mud to the lime kiln [4,5,7,8]. These, in turn, may have an adverse effect on ring formation in the lime kiln, total reduced sulfur (TRS) emissions, and kiln thermal efficiency [9]. Since the presence of free lime in lime mud is indicative of overliming, many mills regularly monitor and control the free lime content in lime mud.

In our laboratory, we analyzed numerous lime mud samples from kraft pulp mills over the years. The free lime contents were consistently found to be low, < 3 wt%  $\text{Ca(OH)}_2$ , even for mills where overliming was suspected to cause problems in causticizing plants and lime kilns. This finding has been puzzling, since if overliming were to be blamed for the problems, why didn't the lime mud at these mills contain an elevated level of free lime? Could the free lime be so reactive that it reacted with  $\text{CO}_2$  in air to form  $\text{CaCO}_3$  during the sample transportation and storage? Could such a small amount of  $\text{Ca(OH)}_2$  be sufficient to cause problems? And if so, why don't all mills have problems?

A systematic study was therefore conducted to address these questions. The study involved i) reviewing the validity of two main analytical methods that are currently used to determine the free lime content, ii) conducting field studies at two kraft pulp mills to examine how the free lime content changes as the lime mud is processed through their causticizing plants, and iii) conducting laboratory studies to examine the effects of liming ratio and mud washing on free lime content. This paper discusses the methods used in this study, the main results obtained, and their practical implications.

## FREE LIME ANALYSIS METHODS

No method for free lime analysis is listed in the current testing standards of TAPPI, PAPTAC, and SCAN. However, from the information and analytical procedures that we obtained from various pulp mills and laboratories, there appear to be two methods available for determining the free lime content in the lime mud. One is the "ammonium chloride ( $\text{NH}_4\text{Cl}$ )" method, which is used mostly in mill laboratories, and the other is the "thermal decomposition (TD)" method, which is used more often in commercial and research laboratories.

## *NH<sub>4</sub>Cl method*

This method appears to have originated from ASTM Standard C25 "Standard Test Methods for Chemical Analysis of Lime-stone, Quicklime, and Hydrated Lime" and ASTM Standard C114 "Standard Test Methods for Chemical Analysis of Hydraulic Cement" for determining the  $\text{Ca(OH)}_2$  content in various products in the lime and cement industries. It is not known, however, when it was introduced to the pulp and paper industry. The procedures involve four main steps: a) dissolving the free lime in the lime mud in a dilute solution of  $\text{NH}_4\text{Cl}$  to form soluble calcium chloride ( $\text{CaCl}_2$ ) and filtering the solution; b) adding ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ) to the filtrate to convert the soluble  $\text{CaCl}_2$  into insoluble calcium oxalate ( $\text{CaC}_2\text{O}_4$ ); c) dissolving the precipitated  $\text{CaC}_2\text{O}_4$  with dilute sulphuric acid to form oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ); and d) titrating the formed  $\text{H}_2\text{C}_2\text{O}_4$  acid with potassium permanganate ( $\text{KMnO}_4$ ). The free lime content is then calculated based on the amount of  $\text{KMnO}_4$  consumed.

While different mills adopt a slightly different version of the method, the concept is basically the same. The main reactions involved in the previously described four steps are:

- a)  $\text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2\text{NH}_4\text{OH}$
- b)  $\text{CaCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 + 2\text{NH}_4\text{Cl}$
- c)  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{C}_2\text{O}_4 + \text{CaSO}_4$
- d)  $5\text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 10\text{CO}_2 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}$

The method, in essence, uses  $\text{NH}_4\text{Cl}$  to dissolve free lime and separate it from the mud as soluble  $\text{CaCl}_2$ , and then uses a series of reactions that follow to determine the amount of the dissolved  $\text{CaCl}_2$ . For each mole of  $\text{KMnO}_4$  consumed in Step d, there would be 2.5 moles of  $\text{CaCl}_2$  present in the filtrate, and hence 2.5 moles of free lime present in the lime mud.

## *TD Method*

Due to its simplicity and accuracy, the thermal decomposition (TD) method is more preferable, particularly in laboratories where muffle furnaces and/or thermogravimetric analyzers (TGA) are available. The method measures the weight loss of the mud sample due to the decomposition of free lime at a temperature between 380°C and 400°C (i.e.  $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$ ) and estimates the amount of free lime. A pure lime mud sample loses 0.243% of its dry mass to thermal decomposition per each wt% of free lime it contains.

## COMPARISON BETWEEN $\text{NH}_4\text{Cl}$ AND TD METHODS

### *Experimental procedures*

In order to determine the validity of the  $\text{NH}_4\text{Cl}$  and TD methods, the free lime contents of two synthetic mud samples were determined using both methods. The samples were prepared by causticizing an aqueous solution of  $\text{Na}_2\text{CO}_3$  (120 g/L  $\text{Na}_2\text{O}$ ) with analytical grade  $\text{CaO}$  at two different liming ratios, 0.85 and 1.0 at 95°C for 1 h; filtering the mud slurry; and then drying the solids at 105°C for 24 h. The dried solids were blended

uniformly before being subjected to free lime analysis. The CE of the resulting liquor was also determined by titrating the liquor with 1 M HCl using an auto-titrator (Metrohm 751 GPD Titrino; Metrohm AG, Herisau, Switzerland). Based on the amount of CaO used in each sample preparation and the causticizing efficiency of the resulting liquor, the free lime contents in these synthetic mud samples were calculated. The results are shown in the column labelled “Theoretical Value” in **Table I**. The synthetic mud sample #1 contained 4.1 wt%  $\text{Ca(OH)}_2$  while the synthetic mud sample #2 contained a much higher free content, 13.1 wt%  $\text{Ca(OH)}_2$  due to the larger amount of CaO used in its preparation.

For the TD method, the simultaneous thermogravimetric/differential scanning calorimetric analyzer (TGA/DSC, Model SDT Q600; TA Instruments, New Castle, DE, USA) available in our laboratory was used. The procedure involved placing 10 mg of a dry mud sample in the analyzer and heating it from room temperature to 900°C at a heating rate of 20°C/min, while continuously monitoring the sample weight. The analyzer was calibrated against the decomposition temperature and corresponding weight loss of analytic grade chemicals:  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$ . In all TD tests, air was passed through the analyzer at a rate of 100 mL/min to purge any released gases (mostly  $\text{CO}_2$ ) from the sample. The weight loss of the sample at 380°C–400°C and the decomposition temperature of  $\text{Ca(OH)}_2$  was used to calculate the free lime content. The results are shown in the column labelled “TD Method” in Table I.

For the  $\text{NH}_4\text{Cl}$  method used in this study, the procedure involved adding 10 g of dried synthetic lime mud to a glass beaker that contained 100 mL of deionized water to produce a mud-water slurry. Subsequently, 10 g of  $\text{NH}_4\text{Cl}$  was added to the beaker and the slurry was stirred for a standard reaction time of 30 min and then filtered. The filtrate was placed in another glass beaker and heated on a hot plate. As the filtrate was about to boil, 2 g of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  was added to the beaker to precipitate  $\text{Ca}_2\text{C}_2\text{O}_4$ , which was allowed to settle for 10 min before being collected and washed. A sufficient amount (2 to 10 mL) of 4N sulfuric acid was then used to completely dissolve the washed  $\text{Ca}_2\text{C}_2\text{O}_4$  precipitate. The solution was then titrated with 0.1N  $\text{KMnO}_4$  to a faint pink end point. From the

amount of  $\text{KMnO}_4$  consumed, the amount of free lime in the synthetic mud was calculated. The results are shown in the column labelled “ $\text{NH}_4\text{Cl}$  Method” in Table I.

Table I also shows the free lime analysis results for two actual lime mud samples obtained from a kraft mill (Mill A). One was collected from the white liquor pressure filter and the other was from the lime mud pre-coat filter. For each sample tested in this study, the procedure was repeated 3 to 5 times. The reproducibility was found to be good, with a typical error of about +/- 3% of the average values.

Note that although the free lime content in lime mud is customarily expressed as wt% CaO, this expression cannot be correct since CaO always reacts with water to form  $\text{Ca(OH)}_2$ , and thus, free lime can exist in the lime mud only as  $\text{Ca(OH)}_2$ , not CaO. Therefore, in this study we choose to express the free lime content as wt%  $\text{Ca(OH)}_2$  to avoid further confusion. Since wt%  $\text{Ca(OH)}_2$  is essentially the same as 56/74 (or 0.76) wt% CaO, it can be readily converted into wt% CaO by multiplying the value by 0.76.

### Result comparison

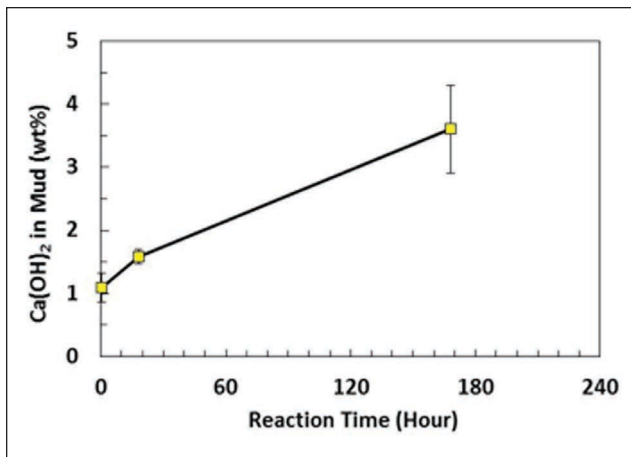
As shown in Table I, the free lime contents obtained with the TD method for the two synthetic mud samples were 4.5 wt% and 13.2 wt%  $\text{Ca(OH)}_2$ , consistent with the theoretical values, 4.1 wt% and 13.1 wt%  $\text{Ca(OH)}_2$ , respectively. The free lime contents obtained with the  $\text{NH}_4\text{Cl}$  method, however, were 0.4 wt% and 0.7 wt%  $\text{Ca(OH)}_2$ , significantly lower than the theoretical values. These results suggest that the TD method was good and reliable, whereas the  $\text{NH}_4\text{Cl}$  method was poor and erroneous.

Similar results were found in the case of actual lime mud samples from Mill A. The TD method showed that the mud sample collected from the white liquor pressure filter contained 7.2 wt%  $\text{Ca(OH)}_2$ , while the mud sample collected from the pre-coat filter contained only 3.5 wt%  $\text{Ca(OH)}_2$ . The  $\text{NH}_4\text{Cl}$  method, however, showed that the free lime content in both mud samples were about 1 wt%  $\text{Ca(OH)}_2$ . This seemingly constant and low free lime content in lime mud obtained with the  $\text{NH}_4\text{Cl}$  method may explain why pulp mills often reported little change of free lime content in lime mud, even when they had problems with overliming.

	Theoretical Value, wt% $\text{Ca(OH)}_2$	TD Method, wt% $\text{Ca(OH)}_2$	$\text{NH}_4\text{Cl}$ Method, wt% $\text{Ca(OH)}_2$
Synthetic mud #1	4.1	4.5	0.4
Synthetic mud #2	13.1	13.2	0.7
Mill A WL pressure filter mud	Not available	7.2	0.9
Mill A pre-coat filter mud	Not available	3.5	1.1
Pure $\text{Ca(OH)}_2$ and $\text{CaCO}_3$ mixture	6.5	6.3	5.7
Pure $\text{Ca(OH)}_2$	99.8	98.0	96.5

**I. Free lime contents measured by ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and thermal decomposition (TD) methods (WL = white liquor).**

# LIME MUD



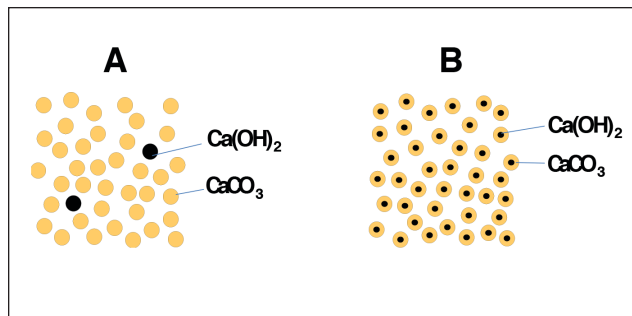
**1. Effect of reaction time between ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and lime mud on the result of the free lime analysis performed on a lime mud collected from Mill A's pre-coat filter, using  $\text{NH}_4\text{Cl}$  method.**

A series of experiments were further performed to investigate why the free lime content obtained with the  $\text{NH}_4\text{Cl}$  method was consistently low. The lime mud sample used in these experiments was also collected from the pre-coat filter at Mill A, but it was not the same mud sample that was shown in Table I. It had a higher free lime content, 5.3 wt%  $\text{Ca(OH)}_2$  as determined by the TD method.

The results of this series of tests are shown in **Fig. 1**. When measured with the  $\text{NH}_4\text{Cl}$  method using the standard reaction time of 30 min, the free lime value was found to be only 1.1 wt%  $\text{Ca(OH)}_2$ , far lower than the value determined by the TD method, 5.3 wt%  $\text{Ca(OH)}_2$ . Even for tests in which the reaction time was substantially extended beyond 30 min, the free lime content was still low: only 1.6 wt%  $\text{Ca(OH)}_2$  after one day (24 h), and 3.7 wt%  $\text{Ca(OH)}_2$  after one week (168 h). These results imply that the  $\text{NH}_4\text{Cl}$  method is unsuitable for determining the free lime content of lime mud. The reaction time of 30 min recommended in this method is simply not sufficient for the reaction between  $\text{NH}_4\text{Cl}$  and the free lime in the lime mud to complete.

In a separate set of experiments, both  $\text{NH}_4\text{Cl}$  and TD methods were used to determine the free lime content of two mixtures of pure chemicals: one contained 6.5 wt%  $\text{Ca(OH)}_2$  and 93.5 wt%  $\text{CaCO}_3$ , and the other contained 99.8 wt%  $\text{Ca(OH)}_2$  and no  $\text{CaCO}_3$ . As summarized in Table I, both methods provided results that were close to the actual mixture compositions, although the TD method appeared to be better than the  $\text{NH}_4\text{Cl}$  method.

The previously mentioned experiments clearly show that while the  $\text{NH}_4\text{Cl}$  method is not suitable for analyzing the free lime content in the lime mud from kraft pulp mills, it can be used for determining the  $\text{Ca(OH)}_2$  content in lime and cement products. This is because in pure  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  mixtures, the  $\text{Ca(OH)}_2$  particles are “completely free” from  $\text{CaCO}_3$  particles, as schematically shown in **Fig. 2A**, and so, it is easier for them to react with  $\text{NH}_4\text{Cl}$ . In the lime mud, how-



**2. Proposed forms of free lime. (A): “Free” lime in a mixture of calcium hydroxide,  $\text{Ca(OH)}_2$ , and calcium carbonate,  $\text{CaCO}_3$ , and (B): “Not-so-free” lime in lime mud.**

ever, the free lime particles are not “so free”, as they are likely to be coated with a thick layer of  $\text{CaCO}_3$  as a result of the causticizing reaction (Fig. 2B). The presence of  $\text{CaCO}_3$  coating layer was postulated by Blackwell [10] and Theliander [11] in the late 1980s based on their studies of the kinetics of the causticizing reaction. The low free lime content in all lime mud samples obtained with the  $\text{NH}_4\text{Cl}$  method in the present study is presumably due to the inability of  $\text{NH}_4\text{Cl}$  to penetrate the  $\text{CaCO}_3$  coating layer to effectively react with the  $\text{Ca(OH)}_2$  in the middle of the lime mud particles.

The TD method also has its own weakness. Since it uses the weight loss of the mud sample caused by the thermal decomposition of  $\text{Ca(OH)}_2$  at around  $380^\circ\text{C}$  to calculate the free lime content, it has an inherent error associated with the presence of magnesium hydroxide ( $\text{Mg(OH)}_2$ ) in the mud.  $\text{Mg(OH)}_2$  decomposes at about  $350^\circ\text{C}$ , which is close to the decomposition temperature of  $\text{Ca(OH)}_2$ . For each wt%  $\text{Mg(OH)}_2$  present, the error will be about 1.3 wt%  $\text{Ca(OH)}_2$ . Therefore, while the TD method is good for free lime analysis, the error associated with the presence of  $\text{Mg(OH)}_2$  must be taken into account.

## FREE LIME IN LIME MUD AT DIFFERENT LOCATIONS

Field studies were conducted to determine the degree of causticizing reaction at different locations in the causticizing plant at two kraft mills. Mill A was equipped with a slaker and four causticizers, a white liquor pressure filter (WLPF), a weak wash pressure filter (WWPF), and a pre-coat filter. The mud slurry from the WLPF was diluted with water before being passed through the WWPF and then the pre-coat filter. Mill B had a similar configuration as Mill A except that it used a white liquor clarifier instead of WLPF, and a conventional mud washer instead of WWPF. Both mills targeted their CE at 80%

All samples were analyzed in our laboratory at the University of Toronto. The slurry samples were filtered to separate the lime mud from the liquor. The liquor was analyzed for  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{S}^{2-}$  concentrations using TAPPI's standard ABC titration method (T624 cm-11 “Analysis of soda and sulfate white and green liquors”), and the results were used to calculate the TTA and CE. The mud was dried at  $105^\circ\text{C}$  for 1 h, then ground



Sample ID	Location	Liquor TTA, g/L Na <sub>2</sub> O	Liquor CE, %	Free Lime in Mud, wt% Ca(OH) <sub>2</sub>
1	Green liquor to slaker	112	11.2	n/a
2	Liquor/mud slurry to #1 causticizer	116	77.1	5.2
3	Liquor/mud slurry from #1 causticizer	118	78.5	5.7
4	Liquor/mud slurry from WLPF	118	79.3	4.1
5	Liquor/mud slurry from WWPF	13.7	72.2	2.5
6	Liquor/mud slurry to pre-coat filter	5.6	71.5	2.3
7	Wet mud from pre-coat filter	-	-	2.3

**II. Analysis results of liquor and mud sampled at different locations at Mill A (TTA = total titratable alkali; CE = causticizing efficiency; WLPF = white liquor pressure filter; WWPF = weak wash pressure filter).**

Sample ID	Location	Liquor TTA, g/L as Na <sub>2</sub> O	Liquor CE, %	Free Lime in Mud, wt% Ca(OH) <sub>2</sub>
1	Green liquor to slaker	117.3	14.6	n/a
2	Liquor/mud slurry to #1 causticizer	114.0	72.7	5.2
3	Liquor/mud slurry from #3 causticizer	119.4	71.8	3.6
4	Liquor/mud slurry from WL clarifier	112.4	79.3	5.9
5	Weak wash	20.9	80.3	-
6	Liquor/mud slurry to pre-coat filter	10.7	94.9	3.1
7	Wet mud from pre-coat filter	-	-	2.9

**III. Analysis results of liquor and mud sampled at different locations at Mill B (TTA = total titratable alkali; CE = causticizing efficiency; WL = white liquor).**

and blended uniformly. Its Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> contents were determined using the previously mentioned simultaneous TGA/DSC analyzer. Due to the possible inclusion of a large amount of sodium compounds in the mud, particularly when the mud was not washed, the free lime content in this series of experiments was expressed as its percentage in calcium compounds only, i.e., Ca(OH)<sub>2</sub>/[Ca(OH)<sub>2</sub>+CaCO<sub>3</sub>] x 100%, so that the results can be compared with one another.

**Table II** summarizes the sampling locations and the analysis results for the study at Mill A. As expected, the green liquor TTA increased from 112 g/L to 116 g/L Na<sub>2</sub>O, remained constant at about 118g/L Na<sub>2</sub>O throughout the causticizing process, and then decreased drastically after the WWPF (Sample #5) where it was only 14 g/L Na<sub>2</sub>O, as more water was added to the system to wash the mud.

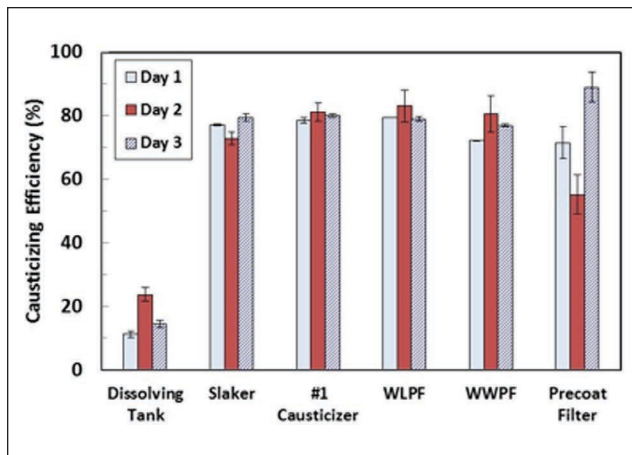
The free lime content in the mud collected from the causticizers was about 5.5 wt% Ca(OH)<sub>2</sub>. It decreased to 2.5 wt% Ca(OH)<sub>2</sub> in the mud collected from the weak wash pressure filter (WWPF) and remained constant at 2.3 wt% Ca(OH)<sub>2</sub> thereafter. This decrease in free lime content was likely due to continued causticizing reaction between Na<sub>2</sub>CO<sub>3</sub> in the li-

quor and the free lime in the mud in a more dilute solution. Lowering the liquor TTA caused the the causticizing reaction (Reaction 2) to shift to the right, enabling the reaction to proceed further. The free lime contents in mud samples to and from the pre-coat filter were the same, 2.3 wt% Ca(OH)<sub>2</sub>, suggesting that diluting and washing the mud on the pre-coat filter did not reduce the free lime content further.

Similar results were obtained for Mill B (**Table III**), which also seemed to achieve its targeted CE of 80%. Comparing the change in liquor CE before and after the slaker to the change in CE before and after the causticizers reveals that the majority of the causticizing reaction completed in the slaker. The degree of completion was estimated to be 96% for Mill A and somewhat lower, 89%, for Mill B.

The high degree of completion of the causticizing reaction in the slaker was further confirmed by the data collected from Mill A for three different days. As shown in **Fig. 3**, the causticizing efficiency, on average, increased drastically from 15% before the slaker to 75% after the slaker, and increased only slightly from 75% to the mill's targeted value of about 80% after the white liquor pressure filter. The results, along with

# LIME MUD



3. Change in liquor causticizing efficiency (CE) as it is processed through Mill A's causticizing plant in 3 different days.

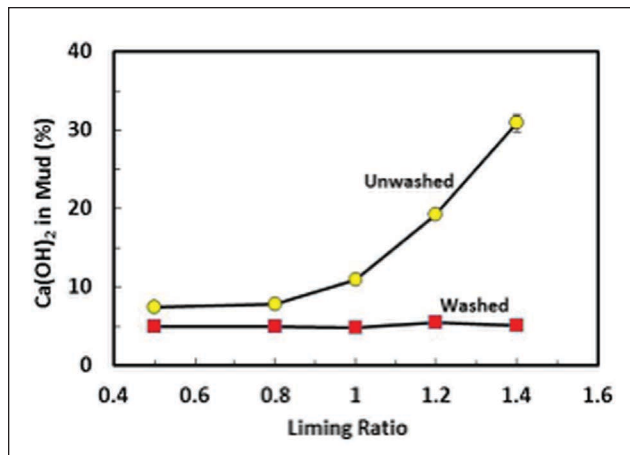
those shown in Tables II and III, suggest that at least for these two mills, over 90% of the causticizing reaction was completed in the slaker.

## EFFECT OF WATER WASHING ON FREE LIME CONTENT

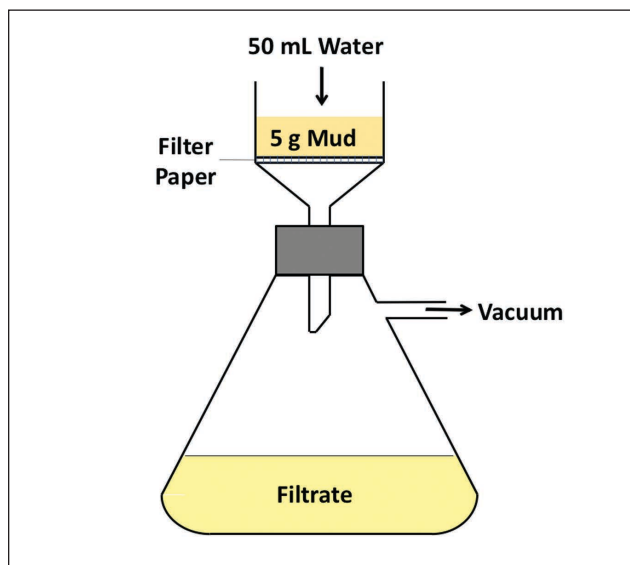
Most pulp mills do their free lime analysis on mud samples collected from the pre-coat drum filter or from the mud conveyor to the kiln, because these are convenient and easy sampling locations. However, since the mud samples at these locations have already been diluted, washed, and dewatered, they may contain less free lime than those collected at a location upstream (i.e., causticizers, white liquor clarifiers, and pressure filters). This is because  $\text{Ca}(\text{OH})_2$  is much more soluble in water than in a strong alkaline solution (white liquor), and some free lime in the lime mud may be washed off during dilution/washing.

In this study, the effect of water washing on free lime content was investigated using synthetic lime mud prepared at various liming ratios ( $\text{CaO}/\text{Na}_2\text{CO}_3$  molar ratio) ranging between 0.5 and 1.4. Two sets of mud samples were prepared: one "unwashed" and the other "well-washed". The preparation procedure for the unwashed mud was the same as that described in the previous section of this paper. The well-washed mud was prepared by adding 1 g of unwashed mud to a glass beaker that contained 100 mL of deionized water, stirring the dilute slurry for 1 h at room temperature, filtering the slurry to obtain the washed mud, and drying it in an oven at 105°C for 24 h. The dried washed mud was well blended before analysis.

Figure 4 shows the free lime content in both unwashed mud and well-washed mud as a function of the liming ratio at which they were prepared. Unwashed mud contained much more free lime than well-washed mud, particularly when prepared under an overliming condition (i.e., liming ratio > 0.8). Well-washed mud, on the other hand, contained less free lime, with an amount that seemed to decrease slightly with an increase in liming ratio. These results may be explained with



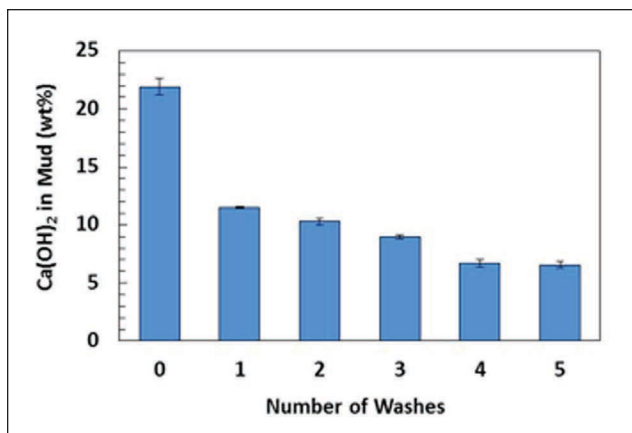
4. Effect of liming ratio on  $\text{Ca}(\text{OH})_2$  content in synthetic mud.



5. Simple setup for mud washing experiments.

the aid of Fig. 2B. Increasing the liming ratio increases the number of mud particles in the slurry, thus resulting in a thinner  $\text{CaCO}_3$  coating layer on the particle surface. This could make it easier for water to penetrate through the thinner  $\text{CaCO}_3$  layer and cause the  $\text{Ca}(\text{OH})_2$  core to dissolve.

In a different set of tests, the synthetic mud produced at a liming ratio of 1.2 was repeatedly rinsed (washed) with water and its free lime content was determined using the TD method. The washing procedure involved placing 5 g of this mud on a filter paper in a vacuum filtration funnel as shown in Fig. 5, pouring 50 mL of deionized water onto the top of the mud sample, applying vacuum to draw the water in the mud slurry through the mud layer and filter paper, and collecting the filtered water in the flask container below. This procedure was repeated five times using the same amount of water (50 mL) each time. A small amount (< 50 mg) of washed mud was collected and analyzed for free lime after each wash. The filtrate was also collected after each wash and analyzed for



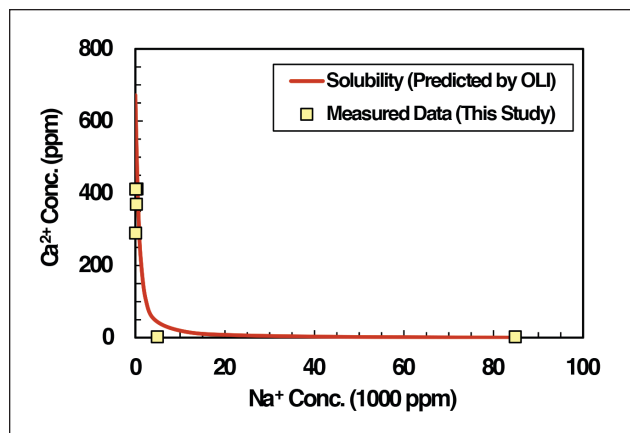
6. Effect of washing on free lime content.

sodium ( $\text{Na}^+$ ) and calcium ( $\text{Ca}^{2+}$ ) concentrations using the Perkin Elmer Analyst 100 atomic absorption spectrometer (PerkinElmer; Waltham, MA, USA) in our laboratory.

The results are shown in **Fig. 6**. Before washing (0 wash), the free lime content in the mud was 22 wt%  $\text{Ca}(\text{OH})_2$ . It decreased to 11.7 wt%  $\text{Ca}(\text{OH})_2$ , almost half of its initial value, after the first wash. It continued to decrease after the second, third, and fourth washes and became levelled off at 6.6 wt%  $\text{Ca}(\text{OH})_2$  after the fifth wash.

Of these numbers of washes, the first wash removed the free lime most effectively. This was probably due to the high initial free lime content in the mud, 22 wt%  $\text{Ca}(\text{OH})_2$ , so that there was more of it available for the water to dissolve and remove. Another important cause of the low free lime as a result of washing was the low  $\text{Na}^+$  concentration in the filtrate (4900 ppm compared to the initial value of 85000 ppm as shown in **Table IV**). This low  $\text{Na}^+$  concentration would allow the causticizing reaction (Reaction 2) to continue to occur and to reach a higher equilibrium CE value, thus converting more free lime into  $\text{CaCO}_3$  during washing.

It is interesting to note from Table IV that while the free lime content decreased almost half of its initial value after the first wash, the  $\text{Ca}^{2+}$  concentration in filtrate was low (about 2 ppm) and the  $\text{Na}^+$  concentration was relatively high (4900



7. Effect of sodium ion ( $\text{Na}^+$ ) concentration on calcium ion ( $\text{Ca}^{2+}$ ) concentrations in the filtrate and on the solubility of  $\text{Ca}(\text{OH})_2$  in water at 25°C.

ppm). This implies that during the first wash, the decrease in free lime content was not a result of its dissolution in water, but rather, a result of the continued causticizing reaction that converted  $\text{Ca}(\text{OH})_2$  into insoluble  $\text{CaCO}_3$ , which stayed with the mud. After the second wash, the  $\text{Na}^+$  concentration in the filtrate decreased substantially to under 400 ppm, while the  $\text{Ca}^{2+}$  concentration increased from 2 ppm to 300-400 ppm. The results clearly shows that more  $\text{Ca}(\text{OH})_2$  dissolved in water as the  $\text{Na}^+$  concentration decreased.

The effect of  $\text{Na}^+$  concentration in the solution on the solubility of  $\text{Ca}(\text{OH})_2$  was also examined under the standard condition of 25°C and 1 atm, using an advanced thermodynamic program, the OLI Stream Analyzer Version 2.0.31 [12]. The program has been successfully used in our laboratory to predict the solubility of recovery boiler precipitator ash in water under various conditions [6,13], and the formation of pirssonite under various causticizing conditions [14].

**Figure 7** shows the effect of  $\text{Na}^+$  concentration in the solution on the solubility of  $\text{Ca}(\text{OH})_2$ . The data points are the actual measurements obtained in this study as shown in Table IV. The solid curve is the solubility of  $\text{Ca}(\text{OH})_2$  predicted by OLI. The increase in  $\text{Ca}^{2+}$  concentration in the filtrate observed in the washing experiments is consistent with the increase in solubility of  $\text{Ca}(\text{OH})_2$  in water with decreasing  $\text{Na}^+$  concentration. As the mud washing process proceeds, the  $\text{Na}^+$  concentration in the solution decreases, allowing more free lime to dissolve. Once the causticizing reaction has reached equilibrium, no further  $\text{Ca}(\text{OH})_2$  can be converted into  $\text{CaCO}_3$  which has a much lower solubility. This means that at low  $\text{Na}^+$  concentrations (< 400 ppm), the dissolution of  $\text{Ca}(\text{OH})_2$  in water becomes the main mechanism for the deletion of free lime in lime mud.

## SUMMARY

A systematic study was conducted to investigate the validity of the two main methods, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and thermal decomposition (TD), used for determining the free-lime or  $\text{Ca}(\text{OH})_2$  content in lime mud. The results show that:

Number of Washes	$\text{Na}^+$ Concentration in Filtrate, ppm	$\text{Ca}^{2+}$ Concentration in Filtrate, ppm
0	85000	2
1	4900	2
2	356	412
3	219	370
4	67	411
5	38	290

IV. Sodium ion ( $\text{Na}^+$ ) and calcium ion ( $\text{Ca}^{2+}$ ) concentrations in the filtrate.

# LIME MUD

1. The  $\text{NH}_4\text{Cl}$  method is not suitable for determining the free lime content in lime mud, due likely to the inability of  $\text{NH}_4\text{Cl}$  to react quickly with  $\text{Ca}(\text{OH})_2$ .
2. The TD method is accurate and good for lime mud samples that contain no or little  $\text{Mg}(\text{OH})_2$ . For lime mud that has a high  $\text{Mg}(\text{OH})_2$  content, the error associated with the presence of  $\text{Mg}(\text{OH})_2$  must be taken into account. For each wt%  $\text{Mg}(\text{OH})_2$  present, the error will be about 1.3 wt%  $\text{Ca}(\text{OH})_2$ .
3. Mud washing can significantly lower the free lime content due to the continuing occurrence of the causticizing reaction, and to a lesser extent, the increased solubility of  $\text{Ca}(\text{OH})_2$  in water as the  $\text{Na}^+$  concentration decreases.
4. Pulp mills typically perform their free lime analysis on mud samples collected from pre-coat filters, which have been washed; the resulting free lime value is usually low.
5. The combined use of  $\text{NH}_4\text{Cl}$  method and washed mud samples for free lime analysis inevitably results in a low free lime value that cannot be used to assess the extent of overliming in the causticizing plant. There is therefore a need for a new method that can effectively and quickly determine the free lime content. **TJ**

## ACKNOWLEDGEMENTS

This work was conducted as part of the research program on "Increasing Energy and Chemical Recovery Efficiency in the Kraft Process - III," jointly supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and a consortium of the following companies: Andritz, AV Nackawic, Babcock & Wilcox, Boise, Carter Holt Harvey, Celulose Nipo-Brasileira, Clyde-Bergemann, DMI Peace River Pulp, Eldorado, ERCO Worldwide, Fibria, FP Innovations, International Paper, Irving Pulp & Paper, Kiln Flame Systems, Klabin, MeadWestvaco, StoraEnso Research, Suzano, Tembec, Tolko Industries, and Valmet.

## LITERATURE CITED

1. Cornell, C.F., in *Chemical Recovery in the Alkaline Pulping Processes* (R.P. Green and G. Hough, Eds.) 3rd edn., TAPPI PRESS, Atlanta, GA, USA, 1987, pp. 119-152.
2. Grace, T.M., in *Pulp and Paper Manufacture, Volume 5. Alkaline Pulping* (M.J. Kocurek, T.M. Grace and E. Malcolm, Eds.), 3rd edn., Joint Textbook Committee of the Paper Industry, TAPPI PRESS, Atlanta, 1989, pp. 566-573.
3. Lindberg, H., and Ulmgren, P., *Tappi J.* 69(3): 126(1986).
4. Dorris, G.M. and Allen, L.H., *J. Pulp Pap. Sci.* 3(3): J99(1987).

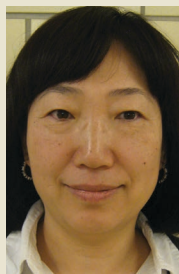
## ABOUT THE AUTHORS

We chose this topic to research because despite the fact that a high free lime content in lime mud is a good indicator of overliming in the causticizing plant operation, the conventional ammonium chloride ( $\text{NH}_4\text{Cl}$ ) method used by many kraft mills for analyzing free lime consistently provides a low value that cannot be trusted. This research complements previous research by other groups in the late 1980s. The results help greatly improve our understanding of slaking and causticizing reactions and explain why the commonly used  $\text{NH}_4\text{Cl}$  method does not work well.

Although the conventional methods for free lime measurement have not been standardized, many pulp mills use them as a standard method. The most challenging aspect of this research is, therefore, to provide a clear explanation for the shortcomings of these common methods. We addressed this by carrying out repeated laboratory and field tests to confirm the results and by using chemical principles to explain the findings.

We discovered that previous research findings and methodologies may need reevaluation, even though they have been widely used by the industry. The most surprising finding was that both the lime mud sampling location and the free lime analytical procedure are not suitable for the free lime analysis.

Mills should replace the  $\text{NH}_4\text{Cl}$  method with the thermal decomposition method for their free lime analysis until a better method is available. Also, the



Mao



Ren



Tran

free lime analysis should be done on lime mud samples collected before filters and washers in order to minimize the effect of water washing on free lime content.

Our next step is to develop a more rapid and more reliable method for free lime measurement and incorporate the method into an online monitoring system for improving the causticizing plant operation.

Mao is senior research associate, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada. Ren is research engineer, Sensors and Controls Group, FP Innovations, Vancouver, BC, Canada. Tran is Frank Dottori professor of Pulp and Paper Engineering, Department of Chemical Engineering and Applied Chemistry, and director, Pulp and Paper Centre, at the University of Toronto. Email Tran at [honghi.tran@utoronto.ca](mailto:honghi.tran@utoronto.ca).



5. Dorris, G.M., *J. Pulp Pap. Sci.* 19(6): J256(1993).
6. Saiedi, S., Tran, H.N., and Papangelakis, V.G., *TAPPI J.* 8(3): 21(2009).
7. Sanchez, D.R., "Recausticizing — Principles and practice," *Course Notes - Kraft Recovery Short Course*, TAPPI PRESS, Atlanta, 2008.
8. Azgomi, F., Farnood, R., and Tran, H.N., "Effects of liming ratio on lime mud settling and filterability," *PEERS Conf.*, TAPPI PRESS, Atlanta, 2010.
9. Tran, H.N., "Lime kiln chemistry and effects on kiln operations," *Course Notes - Kraft Recovery Short Course*, TAPPI PRESS, Atlanta, 2010, Session 2-3.
10. Blackwell, B., *Pulp Pap. Can.* 88(6): T181(1987).
11. Theliander, H., *Nord. Pulp Pap. Res. J.* 3(2): 55(1988).
12. OLI Systems Inc. Available [Online] <http://www.olisystems.com/> <14July2015>.
13. Saturnino, D. and Tran, H.N., *TAPPI J.* 8(5): 26(2009).
14. Zakir, T., Tran, H.N., and Papangelakis, V.G., *TAPPI J.* 12(7): 33(2013)

## TAPPI eLearning: Featuring Company-Wide Solutions

Get your new hires and mill employees updated and qualified with the most current, in-depth e-Learning Courses available to the Pulp, Paper and Tissue industries. Each provides maximum flexibility to meet your needs.

### COURSES THAT MEET YOUR FACILITY'S NEEDS:

- Each Individual Course Can Be Customized
- Include Mill-Specific Equipment and Process Information
- Vary the Lecture Content and Length
- Create Different Content Learning Levels to Meet Your Training Needs

#### PULPING

- Wet End Chemistry
- Paper Coating Technology
- Paper Machine Optimization

#### CHEMICAL RECOVERY

- Chemical Recovery and Environmental Control

#### MILL WIDE SYSTEMS

- Pulp Manufacturing Technology
- Paper Manufacturing Technology
- Tissue Manufacturing Technology
- Pulping Laboratories
- Paper and Board Testing Laboratories
- Technology and Science of Paper Recycling



View a complete list of course descriptions and pricing information at  
[www.tappi.org/eLearning](http://www.tappi.org/eLearning)