Fate of phosphorus in the recovery cycle of the kraft pulping process

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ABSTRACT: The accumulation of nonprocess elements in the recovery cycle is a common problem for kraft pulp mills trying to reduce their water closure or to utilize biofuels in their lime kiln. Nonprocess elements such as magnesium (Mg), manganese (Mn), silicon (Si), aluminum (Al), and phosphorus (P) enter the recovery cycle via wood, make-up chemicals, lime rock, biofuels, and process water. The main purge point for these elements is green liquor dregs and lime mud. If not purged, these elements can cause operational problems for the mill.

Phosphorus reacts with calcium oxide (CaO) in the lime during slaking; as a result, part of the lime is unavailable for slaking reactions. The first part of this project, through laboratory work, identified rhenanite ($NaCa(PO_4)$) as the form of P in the lime cycle and showed the negative effect of P on the availability of the lime. The second part of this project involved field studies and performing a mass balance for P at a Canadian kraft pulp mill.

Application: This paper provides mills with an overview of phosphorus (P) in one mill, as well as some new experimental data, to help understand the P distribution in kraft pulp mills. This can be useful for mills evaluating P inputs and purges.

Phosphorus (P) exists as phosphate in green and white liquors [1]. When lime is added to the green liquor, phosphate ions in the green liquor can react with the calcium in the lime. The resulting P compound in the lime mud has low solubility in green and white liquors, so P will build up in lime over time as it picks up phosphate from the green liquor [1,2]. As a result, the part of the lime that is bound to phosphorus becomes unreactive in the slaking reaction and reduces the availability of lime [1,2]. Ulmgren and Rådeström claimed that concentrations of 1 wt% phosphorus in the lime can decrease the available calcium oxide (CaO) in lime by 5 wt% [1]. The fate of phosphorus in the lime cycle is of special interest, particularly as mills look at introducing biofuels to the lime kiln.

Previous studies have shown that hydroxyapatite ($Ca_5(PO_4)_3(OH)$), also known as HAP, can form when calcium (Ca) is added to alkaline solutions containing phosphate, but not carbonate [3,4]. However, if sodium ion (Na^+) and carbonate (CO_3^{2-}) are present in the alkaline solution (such as in green and white liquors), these ions can partially replace calcium and phosphate in the HAP structure and form a compound containing Na^+ and CO_3^{2-} ions, which is referred to as CAP [5-7].

Ulmgren and Rådeström studied the hydroxyapatite composition of Ca/P precipitates in green and white liquors to determine the mechanisms involved in calcium phosphate precipitates from green and white liquors, and to investigate the possibility of lowering calcium phosphate concentration in the alkaline solutions of the recovery cycle [1,2]. They reported that if the total molar ratio of Ca/P in the solution is less than 0.5 mol/mol, the precipitates mainly consist of HAP, but when the total molar ratio of Ca/P is increased to 1.7 mol/mol, CAP becomes the main component in the precipitates from green and white liquors [2]:

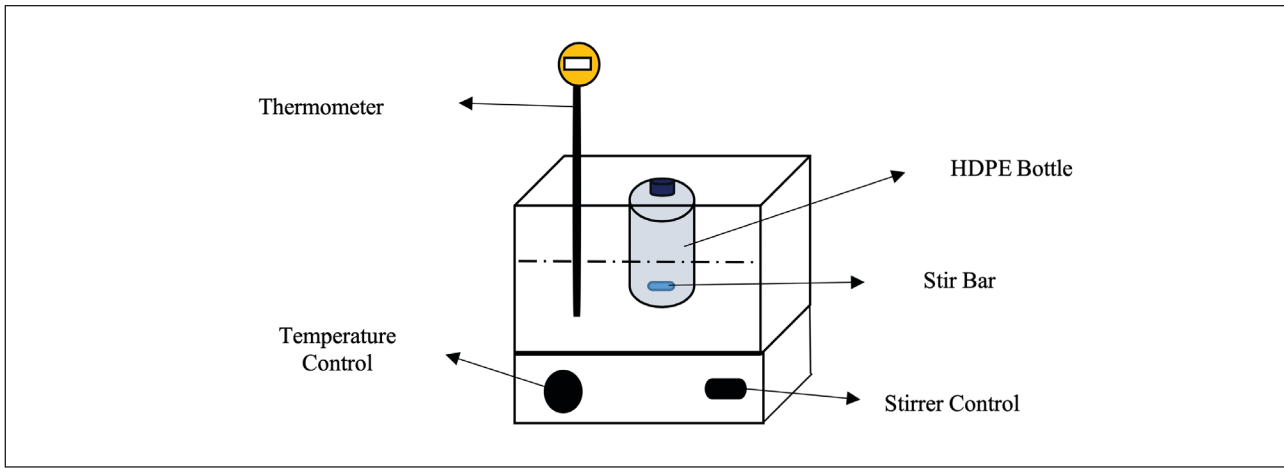
$$Ca_{9\pm0.5}\ Na_{1\pm0.5}\ (CO_3)_{1\pm0.5}\ (OH)_{2\pm0.5}\ (PO_4)_{5\pm0.5}$$
if Ca/P (molar ratio) < 0.5

$$Ca_{8.5\pm0.5}\ Na_{1.5\pm0.5}\ (CO_3)_{2\pm0.5}\ (OH)_{2.5\pm0.5}\ (PO_4)_{4\pm0.5}$$
if Ca/P (molar ratio) ≥ 1.7

In practice, the Ca/P mole ratio will always be much higher than 1.7 mol/mol. Another important conclusion of their study was that they stated that sodium (Na) in the CAP is part of the crystal structure and is not washable [2].

There are some mass balance studies for phosphorus in the literature [8,9]. Salmenoja et al. [9] performed an overall mass balance (inputs and outputs) for phosphorus for five Finnish kraft pulp mills (only the complete results for one mill was shown); they found that the primary inputs of P into the recovery cycle are wood and biosludge combusted in the recovery boiler and that the main output of P is in the lime cycle via slaker grits [9]. Another P mass balance was done by Taylor and McGuffie [8] for a Canadian kraft pulp mill; they found the main inputs of P are the wood and fuel oil in the lime kiln, and the main purge points are the precipitator catch to the sewer and slaker grits.

In this project, P was loaded into lime by successive recausticizing cycles in the lab. The form of P in this lime was determined by X-ray diffraction (XRD). As a part of this work, a complete phosphorus mass balance was done for



1. Schematic of the experimental apparatus (HDPE = high-density polyethylene).

a Canadian kraft pulp, and the concentration of soluble and insoluble P in the recaust streams was determined.

METHODOLOGY

Laboratory experiments

Six slaking/calcining cycles were carried out with a mill green liquor doped with 30000 mg/L sodium phosphate (equivalent to P concentration of 5672 mg/L). The high sodium phosphate addition ensured that the lime could take up sufficiently high amounts of phosphorus in less than 10 slaking cycles and be analyzed using XRD. All slaking/causticizing reactions were done in a 500 ml high-density polyethylene (HDPE) bottle with a magnetic stirrer at 95°C ± 2°C. Lime mud produced after each cycle was washed using 2 to 3 stages with the amount of water equivalent to the amount of green liquor used for slaking. Then, it was calcined at 1200°C ± 20°C to regenerate lime. This lime was then added to a fresh batch of the doped green liquor. **Figure 1** shows a schematic of the experimental setup.

Lime availability after each cycle was measured using a standardized lime analysis method (TAPPI Standard Test Method T 617 cm-84 "Analysis of lime"). Samples were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the P/Ca ratio and the sodium content. After each cycle, lime and lime mud were analyzed by XRD to determine the phosphorus compounds. Furthermore, thermogravimetric analysis (TGA) was done on lime and lime mud to find the thermal stability of the phosphorus compound formed.

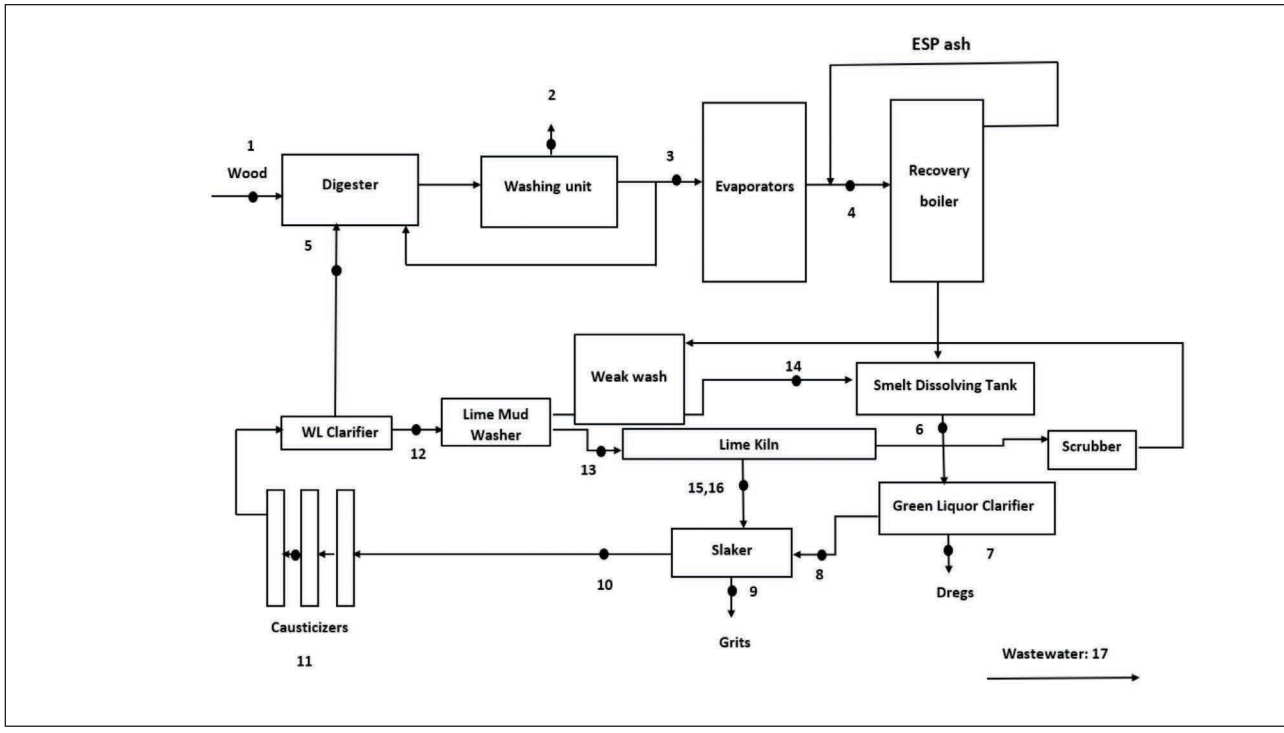
Effect of lime mud washing on phase identification

In order to confirm that the sodium in lime was due to rhenanite rather than entrained sodium compounds, a series of washing experiments were done on a lime mud sample. In this experiment, the first slaking/calcining cycle was repeated. Lime mud was washed with deionized water in multiple stages as before, but this time with more stages (5 instead of 3) and more water in each washing stage (in total, more than the equivalent to the amount of green liquor used in the slaking/causticizing cycle: 250 ml green liquor [GL] for slaking and 350 ml wash water). The lime mud and washed solutions were analyzed by ICP-OES to find sodium levels after each washing stage.

Mill studies

A sampling campaign was carried out at a Canadian pulp mill. The mill uses softwood (equal mix of spruce and pine) for pulping. The annual pulp production rate is 182500 a.d. metric tons/year. The sampling campaign contained 17 sampling points, which are shown in **Fig. 2** and listed in **Table I**.

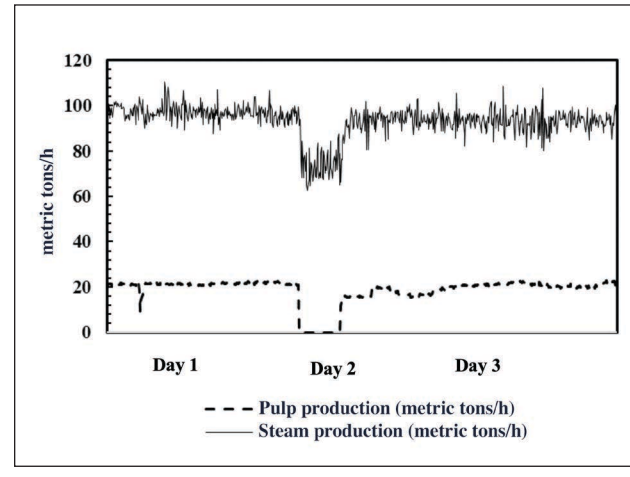
Figure 3 shows the recovery boiler steam production and the mill's pulp production rate during the three days of sampling. These parameters are used to determine the variability of process conditions during the sampling campaign. The digesters went down for about 5 h at the beginning of day 2, so the rate of black liquor combustion was slowed down during this period, but not stopped. The recovery cycle kept running, and the data for that 5 h was not used for mass balance calculations. In all other times, the mill operations were reasonably steady during the sampling campaign, with no significant fluctuations in tank volumes. Flow rates of process streams were taken from the mill's data acquisition historian. The average flow rates of almost 17 h were used for the balance calculations for each day, except for the second day when 12 h of data were used for the flows around the digester because of the reason discussed previously. Clarified green liquor flow rate was adjusted to balance the sodium mass flow in green and white liquors. Also, weak black liquor flow rate was adjusted to balance the black liquor flow rate on a dry solid basis. The average flow rate for each day was used in the balance of the two separate sample rounds. So, for day 2, with two separate sample rounds, the difference in flows



2. Schematic of the recovery and fiber line of the mill (WL = white liquor; ESP = electrostatic precipitator).

Sample No.	Description
1	Wood chips (once a day)
2	Pulp and carryover (liquid remained in the pulp after washing)
3	Weak black liquor
5	White liquor to the digesters
6	Raw green liquor before green liquor clarifier
7	Green liquor dregs
8	Clarified green liquor
9	Slaker grits
10	White liquor after the slaker
11	White liquor between causticizers 2 and 3
12	Clarified white liquor to lime mud washer
13	Lime mud off the lime mud washer
14	Weak wash
15	Hot lime from the lime kiln
16	Lime rock (only one sample)
17	Wastewater (once a day)

I. Sampling points.



3. Steam and pulp production rates during the sampling period (metric tons/h).

of P represents the difference in the concentrations at those two sampling times rather than a difference in the mass flow rate of liquors.

Sample collection and analysis

About 2 kg of wood chips to the digester samples were obtained once a day by the mill operators with a shovel. Wastewater samples were collected from a composite sample pulled by mill personnel once a day. The samples were stored in wide-mouthed HDPE bottles. For each of the other sampling points, samples were collected once on the first day and twice per day on the second and third

days. Weak black liquor and ash-fired black liquor samples were collected using a wide-mouthed HDPE bottle. Ash-fired black liquor samples were collected by the mill operators and stored in a wide-mouthed HDPE bottle. For as-fired black liquor, a weighed amount of deionized (DI) water was added to the bottle prior to pulling the black liquor sample so that the black liquor was diluted. Pulp samples were collected from the washers using a shovel. They were pressed to get samples of the pulp carryover. The pulp carryover samples were collected in wide-mouthed HDPE bottles and pulp samples were stored in the sealed 3 L plastic bags. All bottles were immediately sealed. Once the wood chips, pulp, and black liquor samples were received at the University of Toronto, they were stored at 4°C.

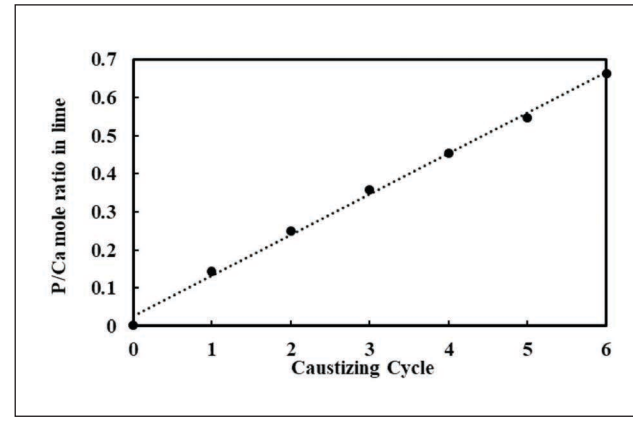
Hot lime samples were obtained directly from the lime kiln and cooled down before storing in the wide-mouthed HDPE bottles. Grits samples were taken using a shovel from the grits storage and stored in sealed 3 L plastic bags. All other liquid samples from the recausticizing plant were taken using a 1 L thermos. The thermos was rinsed with the sample solution at least twice before sample collection. Part of the samples was directly put into analysis vials to determine the total P concentration for the mass balance. The rest of the sample in the thermos was then immediately filtered while still hot using a 1-L filtration flask and cellulose filter paper to get the concentration of soluble P. A portion of this filtered sample was put into vials to later be digested for analysis by ICP-OES. At the mill, the filtered solids were washed with deionized water and dried in an oven at 105°C; afterwards, samples were separated from the mill solutions and stored in 3-L plastic bags.

All liquid and solid samples (except dregs and grits) were digested with 70% nitric acid (HNO_3) at 95°C for 2 h and analyzed by ICP-OES. Prior to digestion, wood samples were air dried and ashed at 540°C. Pulp samples were ashed at 540°C. Dregs and grits samples were ashed at 540°C and prepared using fusion with lithium tetraboride and then analyzed with ICP-OES.

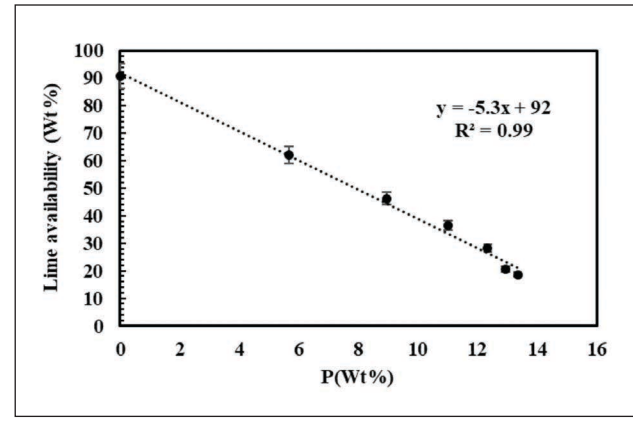
RESULTS

Effect of phosphorus on lime availability

Experiments were carried out to load lime with phosphorus through multiple slaking/causticizing cycles in order to determine the form of the calcium-phosphorus compound and to measure the change in lime availability with P uptake. At each slaking/calcining cycle, lime was added to the green liquor at a liming ratio of 1 ± 0.05. Then, the produced lime was filtered from the produced white liquor, washed, calcined and used in the next cycle. This process was repeated for 6 cycles. After the 6th cycle, the lime availability was too low to continue. The P/Ca molar ratio in the washed lime after each slaking/causticizing cycle was measured using ICP-OES in all cycles and found to increase linearly (**Fig. 4**).

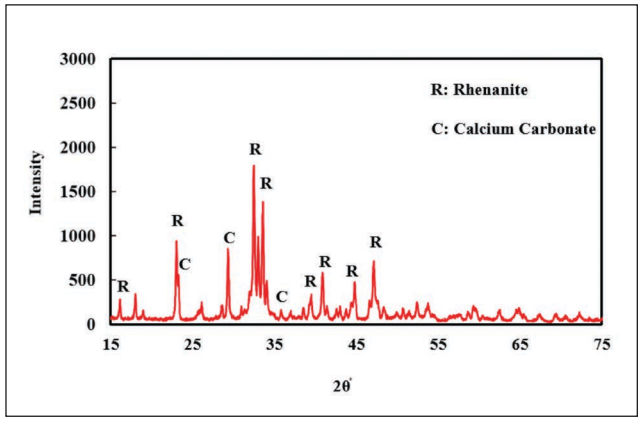


4. Phosphorus/calcium (P/Ca) mole ratio in lime after each slaking/calcining cycle.

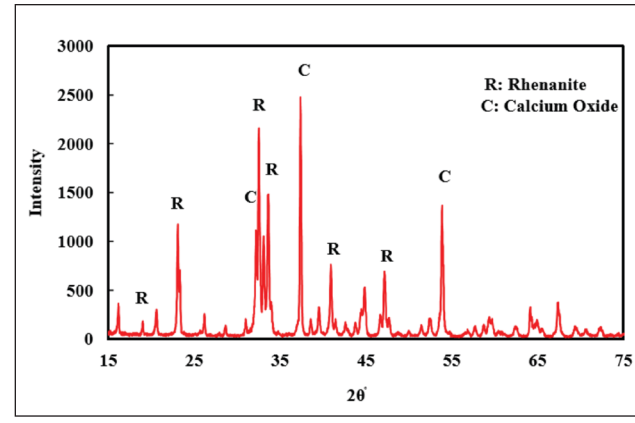


5. Effect of phosphorus (P) content on lime availability. Error bars represent 1 standard deviation based on 6 replicate analyses.

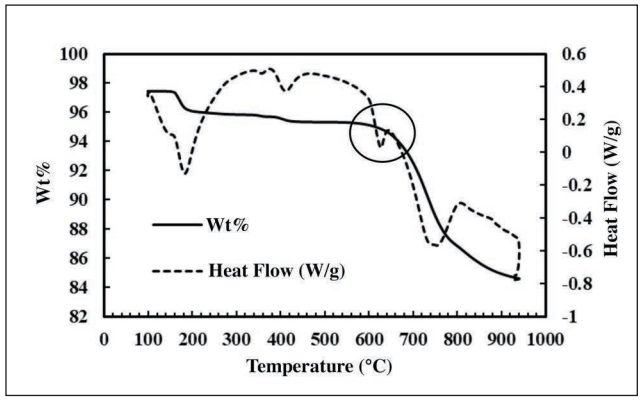
As a result of phosphate uptake by the lime, the amount of lime available for the slaking reaction decreased linearly. The availability of the produced lime after each cycle was experimentally analyzed using TAPPI Standard Test Method T 617 cm-84. The initial lime availability and P (wt%) before the first cycle were 92% ± 2% and 0.18% ± 0.1%, respectively, based on six replicate analyses. The experimental results for lime availability are shown in **Fig. 5**. As shown in Fig. 5, the amount of available lime decreases almost linearly with increasing P (wt%) in the lime. Based on the slope of the trendline for the data in Fig. 5, as the P content in the lime increases by 1 wt%, the availability of the lime decreases by around 5.3 (wt%). The lime availability was also theoretically calculated based on the P (wt%) in the lime and assuming lime only consists of CaO and rhenanite. The theoretical relationship would be a 5.1% reduction in availability for every 1 wt% of P in the lime mud. The reason the measured relationship is slightly higher than the theoretical lime availability might be due to partial blocking of reactive lime by rhenanite or to recarbonation of lime mud immediately following calcination in the experimental conditions.



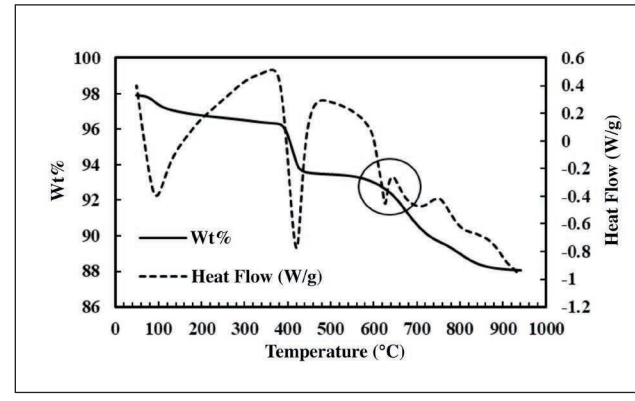
6. X-ray diffraction (XRD) of lime mud after the 6th slaking/calcining cycle. P/Ca molar ratio = 0.59.



7. XRD of lime after the 6th slaking/calcining cycle. P/Ca molar ratio = 0.59.



8. Thermal profile of lime mud after the last cycle. This shows the transformation of α-rhenanite to β-rhenanite between 600°C and 640°C in lime mud (heat loss showing this transformation is circled on the curve).



9. Thermal profile of lime after the last cycle. This shows the transformation of α-rhenanite to β-rhenanite between 600°C and 640°C in lime (heat loss showing this transformation is circled on the curve).

Identification of phosphorus compounds (XRD profiles)

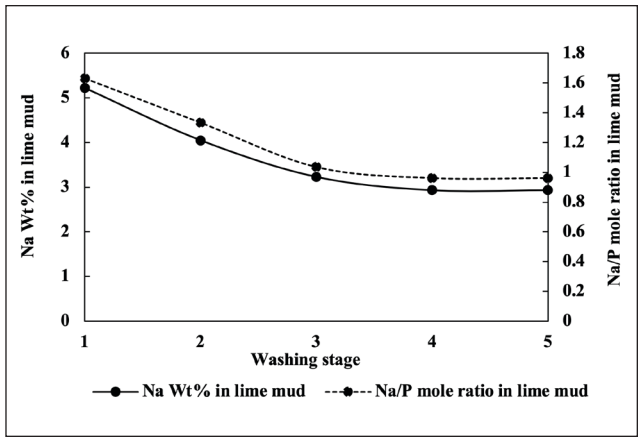
Solid samples after each cycle were analyzed with XRD to identify the Ca-P compounds in the lime and lime mud. The XRD results showed that the Ca-P compound formed in lime and lime mud is rhenanite ($NaCa(PO_4)$). The XRD profiles of the last slaking/calcining cycles are shown in **Fig. 6** and **Fig. 7**. This finding is in contrast to the conclusion of Ulmgren and Rådeström that HAP and CAP could be formed [1,2]. It was not clear how the presence of HAP and CAP were determined in these earlier studies, so it is difficult to compare our results with their conclusions. While the phosphate content in the doped green liquor is much higher than in industrial liquors, it is not phosphate-rich relative to carbonate and hydroxide. The phosphate-to-carbonate molar ratio is only 0.145 and the phosphate-to-hydroxide ratio is 0.408, so it seems unlikely that the high phosphate content of the doped green liquor prohibited the formation of HAP and CAP, and these results would tend to indicate that the form is rhenanite.

Thermal stability of phosphorus compounds (TGA profiles)

Lime and lime mud samples were analyzed by thermogravimetry and differential scanning calorimeter (TGA/DSC) to find the thermal stability of the calcium-phosphorus compounds formed. The TGA profiles for lime and lime mud after the last cycle are shown in **Fig. 8** and **Fig. 9**. A typical thermal profile of lime shows a weight loss between 350°C and 450°C, which corresponds to the decomposition of calcium hydroxide ($Ca(OH)_2$) into CaO and water (H_2O). The theoretical weight loss of H_2O from pure $Ca(OH)_2$ is 24%.

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O$$

A typical thermal profile of lime mud shows two weight losses: first, a weight loss at 350°C–450°C that was described previously; and second, a weight loss between 620°C and 830°C that corresponds to the decomposition of calcium carbonate ($CaCO_3$) into CaO and carbon dioxide (CO_2), and the theoretical weight loss of CO_2 from pure $CaCO_3$ is 44%.



10. Remaining sodium (Na) content in the lime mud after multiple washing stages (primary y-axis) and sodium/phosphorus (Na/P) mole ratio in lime mud after multiple washing stages (secondary y-axis).

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

In addition to the typical peaks expected for lime and lime mud, respectively, the TGA results with high phosphorus contents show an endothermic reaction (with no weight loss) between 600°C and 640°C that was consistent with a crystal structure change of α-rhenanite to β-rhenanite [10].

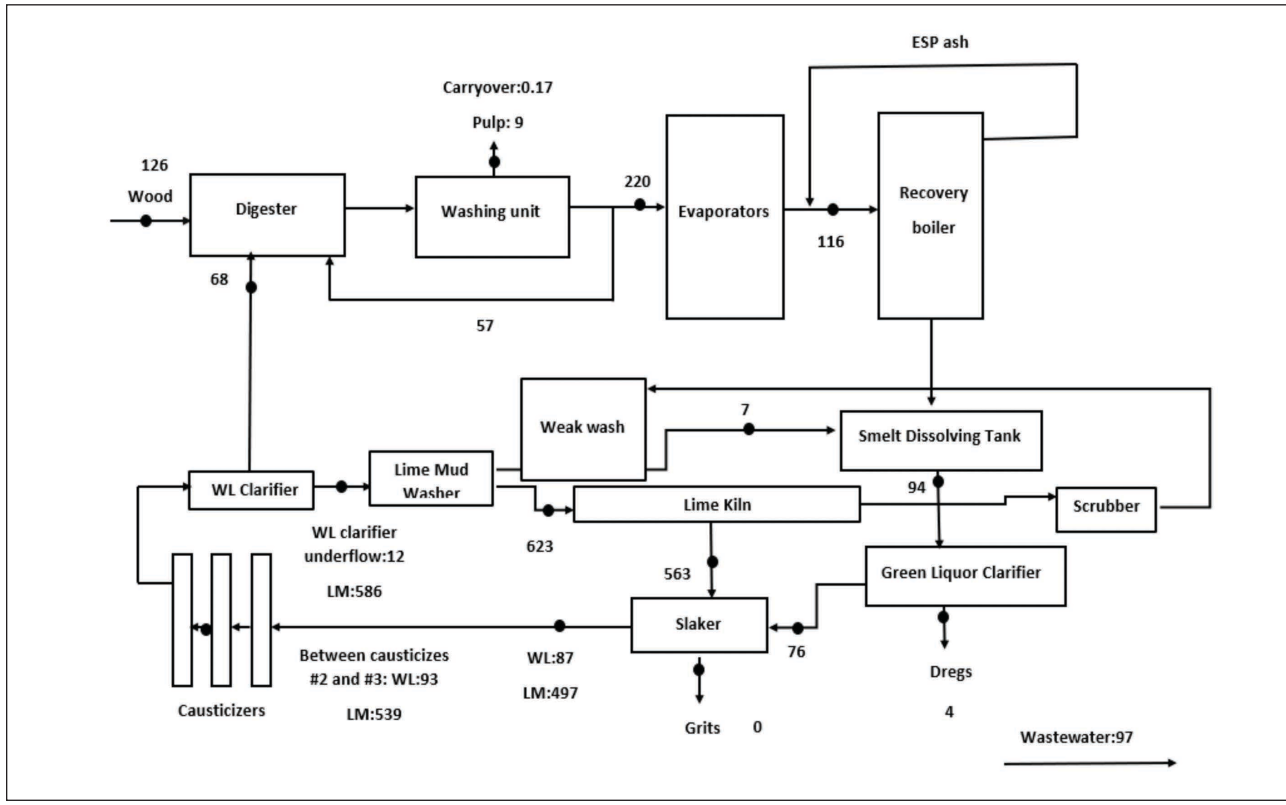
Effect of lime mud washing on phase identification

Figure 10 shows the effect of washing on sodium concentration in the lime mud. As can be seen in Fig. 10, the sodium level in the lime mud decreased from stage 1 to stage 4, after which it became constant. Also, after the fourth cycle, little to no Na was washed from the lime mud. Besides Na, the P concentration in the washed solution was analyzed as well. The results showed no P was washed out in any of the washing stages. This suggests that the washed Na was not from the rhenanite structure. It could be the Na in residual green liquor. Thus, all the remaining Na in the lime mud after washing is bound to P in the rhenanite structure. Figure 10 also shows the molar ratio of Na and P in the lime mud after the 4th washing stage becomes constant and is very close to 1, which is the molar ratio of Na and P in the rhenanite ($NaCa(PO_4)$).This result is in good agreement with the results of a previous study that found Na in the CAP structure is not part of its crystal structure and it is not washable [2].

Mass balance results

The mass balance results of five sampling periods are shown in **Fig. 11** and **Table II**. Results are given on g P/metric tons of a.d. pulp (g P/a.d. metric tons) basis.

As shown in Fig. 11, the main input of P to the recovery cycle is the wood used in pulping. Almost all of the P in



11. The average P flows in the recovery cycle (WL = white liquor; ESP = electrostatic precipitator; LM = lime mud). Units are g P/a.d. metric ton.

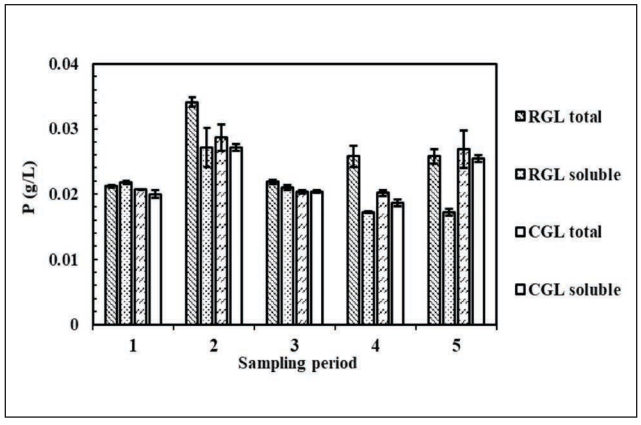
Sample No.	Description	P Average, g P/a.d. metric tons of pulp	P Range, g P/a.d. metric tons of pulp
1	Wood chips	126	118–133
2	Pulp and carryover (liquid remained in the pulp after washing)	Pulp: 9 Carryover: 0.17	Pulp: 8–10 Carryover: 0.08–0.25
3	Weak black liquor	220	157–295
4	As-fired black liquor	116	91–142
5	White liquor to the digesters	68	56–79
6	Raw green liquor before green liquor clarifier	94	75–122
7	Green liquor dregs	4	2–8
8	Clarified green liquor	76	58–100
9	Slaker grits	0	0
10	White liquor after the slaker	White liquor: 87 Lime mud: 497	White liquor: 50–124 Lime mud: 391–594
11	White liquor between causticizers 2 and 3	White liquor: 93 Lime mud: 539	White liquor: 67–134 Lime mud: 486–652
12	Clarified white liquor to lime mud washer	White liquor: 12 Lime mud: 586	White liquor: 8.5–16 Lime mud: 455–762
13	Lime mud off the lime mud washer	623	560–675
14	Weak wash	7	4–12
15	Hot lime from the lime kiln	563	403–747
16	Lime rock	565	–
17	Wastewater	97	82–115

II. Phosphorus (P) content of samples collected at various sampling points.

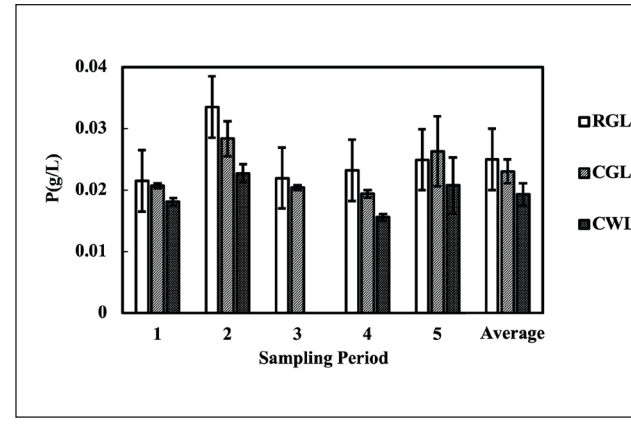
the wood is solubilized during pulping and enters the recovery cycle with the black liquor. Almost half of the P of weak black liquor appears to be volatilized during evaporation and ends up in the evaporator condensates. The possible explanation would be that the organic P-containing compounds of the wood are degrading during pulping to form molecules with a lower molecular weight that are volatilized during evaporation. Unfortunately, the contaminated condensate sample from the evaporator was not collected at the time of the sampling campaign to experimentally prove this hypothesis. However, we did sample the water to the wastewater treatment plant. The evaporator condensates and digester blow gases go to wastewater treatment and the P flows with the wastewater are close to the observed drop in the P in the evaporators.

Karlemo [11] measured P in weak and as-fired black liquor from six kraft pulp mills in Finland. In that work, the author found that P in the as-fired black liquor is higher on a dry solids black liquor than for the weak black liquor. One explanation is that biosludge is added to those liquors; however, the flow of biosludge and P content of the biosludge in those mills was not given, so it is not possible to draw final conclusions about the differences between those results and our study.

Black liquor after evaporation is mixed with electrostatic precipitator ash and then it is burned in the recovery boiler. It appears that perhaps as much as a third of the P in the as-fired black liquor is released during combustion in the recovery boiler. Unfortunately, the electrostatic precipitator ash sample was not collected during the sampling campaign. Assuming that 8% of the Na is volatilized, that there is enough sulfur (S) to balance Na, and that the precipitator ash is only sodium sulfate (Na_2SO_4), the theoretical concentration of P in the precipitator ash would be about 60 mg/kg. An electrostatic precipitator ash sample was received later from the mill and was analyzed for P. The concentration of P in that sample is 16 mg/kg, which is lower than the theoretical value. Karlemo [11] measured P in electrostatic precipitator ash, and she found values between 40 mg/kg and 50 mg/kg [11]. Finnish mills usually operate their recovery boilers at a higher temperatures and solids contents when compared to Canadian mills, so



12. Total and soluble P in raw green liquor (RGL) and clarified green liquor (CGL). Error bars represent 1 standard deviation of 6 replicate analyses of the samples.



13. Total P concentration in liquid samples of the recausticizing plant at each sampling period (RGL = raw green liquor; CGL = clarified green liquor, CWL = clarified white liquor). Error bars represent 1 standard deviation of 6 replicate analyses of the samples.

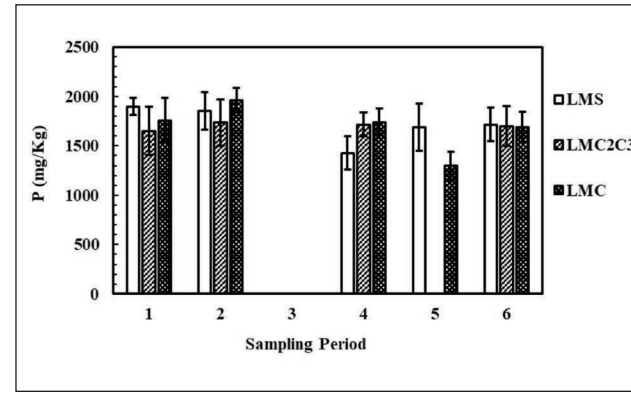
it is acceptable that those values are higher than the measured P concentration in the sample received from the Canadian mill, which fires at a lower dry solids. More work is needed to better understand the fate of P during evaporation and combustion.

The remaining two-thirds of the P in the black liquor after combustion exit the recovery boiler with the smelt and are dissolved in the weak wash to form green liquor in the recausticizing plant. In the recausticizing plant, about 20% to 25% of the phosphorus was picked up by the lime during slaking and recausticizing, whereas the rest ends up in the digester with the white liquor. This will be discussed further in the following sections.

Figure 11 shows the P flows when the mill is on 100% lime mud. If the mill goes to lime rock, the lime rock is added to the kiln instead of to the lime mud. Based on the mill data for the 6 h that they were on 100% lime rock on the night between the first and second sampling periods, the P flow from the addition of lime rock to the lime kiln is 565 g P/metric ton of pulp.

Besides total P in the raw and clarified green liquors, the soluble fraction was also measured to differentiate between soluble and insoluble P. The results are shown in **Fig. 12**.

Based on Fig. 12, about 80% to 95% of the P in the raw green liquor exiting the dissolving tank is soluble, while about 15% to 20% is insoluble. The insoluble fraction is removed with the dregs and the remaining P goes with the green liquor to the slaker. Based on the mass balance results, a little amount of P is purged with scrubber water and green liquor dregs. There was virtually no phosphorus being purged by the slaker grits, which is in contrast with other studies [8,9]. This is likely due to the fact that at this mill the P concentration in the green liquor is quite low, so there is almost no reaction between phosphate ions in the green liquor to the slaker and the lime added to the slaker. Furthermore, the concentration of P in the lime is low. It is the P-containing lime that is unreactive and might



14. Phosphorus concentration in solid samples of the recausticizing plant at each sampling period (LMS = lime mud after slaker; LMC2C3 = lime mud between causticizers 2 and 3; LMC = lime mud after the clarifier). Error bars represent 1 standard deviation of 6 replicate analyses of the samples.

form grits in mills with higher levels of P in the lime.

The fate of P in the recausticizing plant is of special interest. **Fig. 13** and **Fig. 14** show the variability of P concentration in the liquid and solid samples of the recausticizing process, respectively. Between 20% and 25% of the P was picked up by the lime during slaking and recausticizing, Thus, most of the phosphorus entering the slaker with clarified green liquor continued with white liquor to pulping. Uptakes of green liquor P by lime mud has been found to be as high as 70% to 75% of the green liquor P when the concentration of P in the green liquor is around 25 to 65 mg/L [1], but much lower when the concentration is around 20 to 25 mg/L [11]. This difference between our findings and earlier findings may be because the initial P concentration of the green liquor at this mill is low, being only 20 to 30 mg/L. The other reason might be that the lime mud is already at equilibrium, so it did not pick up much P from the green liquor during slaking and causti-

cizing. More work is needed to better understand under what conditions phosphorus is removed from the green liquor by the lime.

The measured total input of P with the wood is 126 g P/a.d. metric ton pulp, and total output from dregs, grits, pulp, and wastewater is 110 g P/a.d. metric ton pulp, with the majority found in the wastewater. Therefore, there is an approximate 13% difference between the total input and output. The electrostatic precipitator in this mill was working highly inefficiently during the sampling campaign, so there might have been some P being released with particulate in the flue gas, but we could not quantify this, as mentioned before. The mass balance results in this mill show very little to no P accumulation because the P level in this mill is quite low in the green liquor, so there is little pick-up by the lime during slaking and causticizing. In other mills with higher P content, the accumulation would most likely happen in the lime mud [2,11].

CONCLUSIONS

The laboratory experiments in this work showed the form of phosphorus in the lime cycle is rhenanite. Additional work will be carried out to better clarify this. Based on the mass balance results, the primary source of P entering the pulp mill comes from wood, and almost all of this P is solubilized during digestion and ends up in the black liquor. Mass balance results suggest that after evaporation, about half of the black liquor P remains in the black liquor and the remainder seems to be volatilized during evaporation

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ABOUT THE AUTHORS

We chose this research topic because the build-up of phosphorous (P) in the lime cycle is one concern for utilization of biofuels in the lime kiln. As mills look to replace fossil fuels with biomass derived fuels, the choice of fuel and technology depends, in part, on the fate of nonprocess elements introduced with the fuel, particularly phosphorous.

This research was complementary to the work of Ulmgren and Rådeström, who studied the form of P in green and white liquor precipitates. The form is important in order to understand and model the distribution between the solid phase and liquid phase during slaking and causticizing. We found a different form for phosphorous lime and lime mud from what they identified.

The most difficult aspect of this work was the low concentration of P in lime and lime mud, making analysis of the form problematic. We addressed this problem by conducting multiple slaking/causticizing/calcining cycles with mill lime and mill green liquor doped with sodium phosphate. This allowed for increased P concentration, making X-Ray diffraction analyses possible.

This research is going to be used as the first step towards building a thermodynamic database that can be used in modeling the distribution of P between the liquid and solid phases. We learned several new things from this work: there appears to be a minimum P concentration in green liquor beyond which the pick up by lime is low; the reaction between P in the green liquor and lime appears to happen later in the slaking/causticizing cycle; and significant amounts of P may be volatilized in black liquor evaporation. We will be conducting more work to follow up on these observations.

The most interesting finding was that the form of phosphorus in the lime and lime mud is rhenanite, which differs from the conclusions of Ulmgren and Rådeström. This work can help mills understand the form of P and its distribution around the recovery cycle. This is particularly useful for mills considering use of biofuels in the lime kiln.

This paper provides mills with an overview of phosphorous in one mill, as well as some new experimental data to help understand P distribution during slaking and causticizing.

The next step is investigating the effects of TTA, sulfidity, and green liquor's P content on the reaction between phosphate in green liquor and the lime during slaking/causticizing.

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and ends up in the evaporator condensates. Unfortunately, this assumption was not experimentally verified because an evaporator condensate sample was not collected. After black liquor combustion in the recovery boiler, about 70% of the black liquor P is retained in the smelt and the remainder is believed to be in the electrostatic precipitator ash. The P in smelt is nearly completely soluble in green liquor. It partially reacts with Ca that comes with the lime during slaking and causticizing to form rhenanite, which reduces the lime availability by 5.3 wt% for every 1 wt% of P. The mill balance indicates that the distribution between soluble phosphorus and phosphorus bound to the lime during slaking and recausticizing is likely a function of P concentration in the green liquor and lime. The remainder of the P enters the digester with the white liquor and ultimately ends up back in the black liquor. **TJ**

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