Factors affecting phosphorus uptake/dissolution during slaking and causticizing

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ABSTRACT: Hydroxide is regenerated in the recovery cycle of kraft pulp mills by the addition of lime (CaO) to green liquor. Phosphate in green liquor can react with the lime during slaking/causticizing. Total titratable alkali (TTA), sulfidity, the concentration of phosphate in the green liquor, temperature, and the liming ratio were all variables explored in this work to determine their influence on phosphorus uptake and dissolution. Experiments were also run in which the lime was slaked before being added to the green liquor to separate reactions with phosphate during slaking and reactions that occur during causticizing. Both reburnt lime and technical grade CaO were used. The experiment results indicate that phosphorus primarily reacts with slaked lime ($Ca(OH)_2$), and that the final concentration of phosphate in the white liquor at the end of slaking and causticizing is nearly independent of the initial concentration of phosphorus and only mildly dependent on the carbonate concentration in the green liquor. There do appear to be differences in the rate at which phosphate reacts with reburnt lime and technical grade CaO, though the reason for this was not determined.

Application: Phosphorus that enters pulp mills with the wood to the digester is ultimately purged from the mill with the purged lime mud. This work can be used by mills to predict how much lime needs to be purged if considering higher phosphorus inputs to the mill through combustion of biomass fuels in the lime kiln or combustion of biosludge with black liquor in the recovery boiler.

Phosphorus, a non-process element in kraft pulp mills, enters the digester with the wood and white liquor [1-3]. Essentially, all of the phosphorus exists with the black liquor to evaporation [2]. The amount of phosphorus entering with the wood depends on the wood species, harvest season, and geographical location [4,5]. Furthermore, different parts of a tree have different concentrations of phosphorus, with the concentration in bark being higher than in the stem wood on a dry mass basis [4,5]. Thus, poor debarking can result in an increase of phosphorus into digestion. Phosphorus is carried through the evaporators with the black liquor to the recovery boiler, and the majority of the phosphorus in the black liquor exits with the smelt and is dissolved in the green liquor [2]. It is this phosphorus that reacts with the lime in the slaking and causticizing process. Other sources of phosphorus in the recovery cycle can be makeup lime, process water, biosludge (10–500 mg/kg dry basis [d.b.]) and biofuels (4–191 mg/kg d.b. with wood and 428–1260 mg/kg d.b. with bark) if burned in the lime kiln [5-8]. The phosphorus concentration in the green liquor of North American and Nordic mills varies between 7–35 ppm and 6–65 ppm, respectively [2,9-12]. One of the explanations for the higher concentration range of phosphorus in the Nordic mills could be the combustion of biosludge with the black liquor in some Nordic mills.

In the recausticizing process, phosphorus reacts with calcium that comes with the lime to form calcium-phosphate compounds, which can reduce the lime availability by almost 5 wt% for every 1 wt% of phosphorus [2,10]. Therefore, mills need to purge some lime mud and purchase fresh lime to maintain their desired lime availability and causticizing efficiency, preventing the formation of deadload in the lime cycle [11]. This incurs costs for the mills in terms of purchasing makeup lime and landfilling of lime mud. Based on the previous work done by the authors of this paper, the form of phosphorus in the lime and lime mud is rhenanite ($NaCaPO_4$) [2]. Others have identified it to be hydroxyapatite ($Ca_5(PO_4)_3OH$) or hydroxyapatite compounds containing sodium ion (Na^+) and carbonate ion (CO_3^{2-}) [13,14] or silicorbenanite [13]. Going forward, we will refer to the phosphorus containing compound in lime and lime mud as rhenanite, based on our earlier findings. As mills explore the prospect of replacing fossil fuels with biomass-derived alternatives, it is important to acknowledge that this shift may lead to a rise in the phosphorus input to the lime cycle. This increase, in turn, contributes to a higher accumulation of phosphorus in the lime mud, given the inherently elevated phosphorus content in biomass compared to fossil fuels. Thus, it is crucial to investigate the factors that affect the formation of dead load in the lime mud as rhenanite in the lime cycle.

Ulmgren and Rådeström [10] studied the effect of total titratable alkali (TTA), temperature, liming ratio, and type of lime (analytical grade vs. reburnt lime) on calcium phosphate precipitation from green liquor. Their investigated ranges were 2.5–5 mol/L Na^+ with different liming ratios (0.05, 0.5, 0.75, and 1.1) at 60°C and 90°C. The initial phos-

phorus concentration in the green liquor was 310 ppm in all the experiments, except for the liming ratio experiment in which it was 62 ppm. Their experiments were conducted by using analytical-grade lime (CaO), with a few conducted with reburnt lime (lime availability = 84%). Based on the results of their study, phosphorus pickup by the analytical-grade lime from the green liquor increased with decreasing TTA and increasing liming ratio. They found that the effect of temperature on calcium phosphate precipitation was small when analytical-grade CaO was used [10]. They showed that the time needed to reach equilibrium for Ca ions when it was added as calcium carbonate ($CaCO_3$) or calcium hydroxide/slaked lime ($Ca(OH)_2$) was a few hours. However, the time that it took for the phosphate ion (PO_4^{3-}) concentration to reach equilibrium in green and white liquors containing excess amount of phosphorus was 30 days and 60 days, respectively. The phosphate ion concentration in the white liquor after 3 h and 60 days was 13.95 and 5.58 ppm, respectively [10]. In another work done by Ulmgren and Rådeström [14], they mentioned that it was difficult to see if the system had reached a true thermodynamic equilibrium due to slow reaction rate. Therefore, they performed a solubility study to find the equilibrium phosphate concentration in green and white liquor. They showed that the time to reach a steady state phosphate concentration in green and white liquors was between 4–20 weeks at different calcium/phosphorus (Ca/P) ratios. The steady state solubility of PO_4 in green and white liquors at 90°C was 95 ppm and 3.72 ppm, respectively [14].

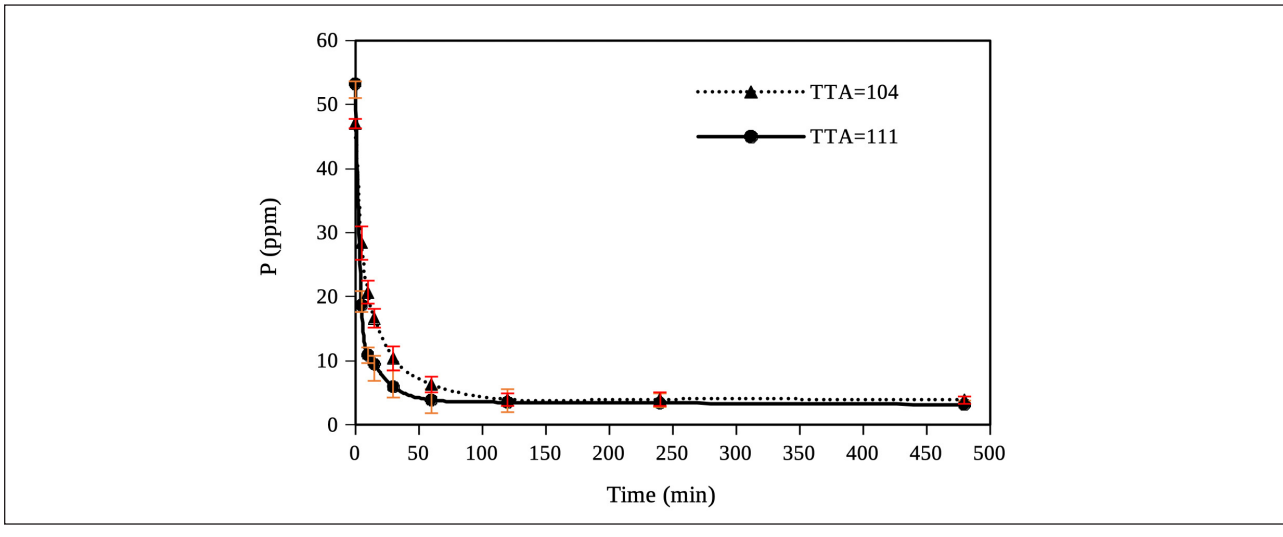
The aim of this work is to further understand the uptake of phosphorus in the lime cycle at mill conditions. The effect of carbonate concentration on rhenanite formation/dissolution is investigated by changing the green liquor's carbonate concentration in two ways: changing TTA at constant sulfidity, and changing sulfidity at constant TTA. The role of slaking and causticizing on phosphorus uptake by lime was investigated by pre-slaking the lime, and, in some experiments, this was followed by addition to green liquor for causticizing to occur. To see the effect of green liquor's phosphorus concentration, experiments were carried out at three different phosphorus concentrations. The effect of liming ratio and lime type were studied by running experiments at different liming ratios and different lime types, respectively. The kinetic and mechanism behind the phosphorus dissolution were also studied for both reburnt lime and technical grade CaO.

EXPERIMENTAL

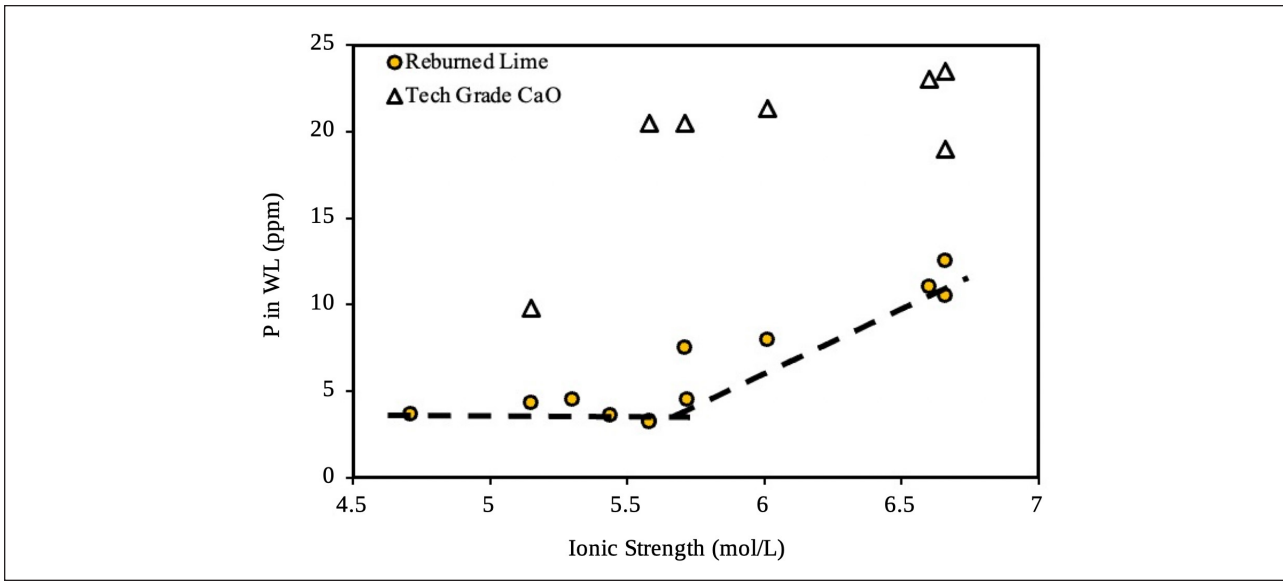
Samples of synthetic green liquors at different TTA, sulfidity, and phosphorus concentrations were prepared using Na_2CO_3 (sodium carbonate, ACS grade, anhydrous, 99.5%), Na_2S (sodium sulfide, technical grade), and Na_3PO_4 (trisodium phosphate, ACS grade, anhydrous, 96%). The Na_2S chemical consisted of a mix of sulfide, sulfite (mostly), sulfate, and thiosulfate (trace amount) due to oxidization. Therefore, the targeted sulfidity was obtained by adding more chemicals (~×1.5–1.7g/L). The concentrations of hydroxide, carbonate, and sulfide were determined by three-point titration with 1 N hydrochloric acid (HCl).

A 2 kg sample of reburnt lime with initial lime availability of (92% ± 2%) was obtained from a Canadian mill and was calcined at 950°C for 2 h prior to each experiment. Technical-grade CaO was also heated up to 550°C prior to the experiments to ensure there was no $Ca(OH)_2$ present. All the slaking/causticizing reactions were done at (95°C ± 2°C) in a water bath that held a 250 mL fluoropolymer (PFA) bottle with a magnetic stir bar. Samples were pulled using a needle attached to a plastic syringe and were filtered using a 0.2 µm polyethersulfone (PES) membrane sterile filter.

Due to a high concentration of sodium ions, samples were diluted with 5% nitric acid prior to being analyzed by



1. Phosphorus (P) concentration in the liquor with low total titratable alkali (TTA) of 111 and 104 g/L sodium oxide (Na_2O) during 8 h of reaction time. Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.



2. Phosphorus (ppm P) in the white liquor (WL) as a function of ionic strength at a liming ratio of 1 for reburnt lime and technical grade lime (CaO). The initial P concentration in the green liquor was 50 ppm.

inductively coupled plasma-optical emission spectrometry (ICP-OES, 213.618 nm). The average concentration variability for phosphorus obtained from ICP-OES measurements for the initial green liquor solutions was ± 3 ppm after applying the dilution factor. Therefore, all concentrations for the stock solutions are reported with ± 3ppm variability.

Unless otherwise stated, the liming ratio for the experiments was one and samples were pulled after 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 120 min, and 240 min. Two initial experiments were carried out for 8 h to make sure that a steady concentration is reached within four hours.

RESULTS AND DISCUSSION

A series of experiments were conducted for 8 h to see when the system reaches equilibrium. These experiments were done at two different TTAs, 104 sodium oxide (Na_2O) g/L and 111 Na_2O g/L; sulfidity = 14 ± 1% (TTA basis); and phosphorus concentration of 50 ± 3 ppm.

Reburnt lime was added to green liquor and was slaked and causticized for 8 h. After 2 h, the concentration of phosphorus in the liquor became constant for these conditions (**Fig. 1**).

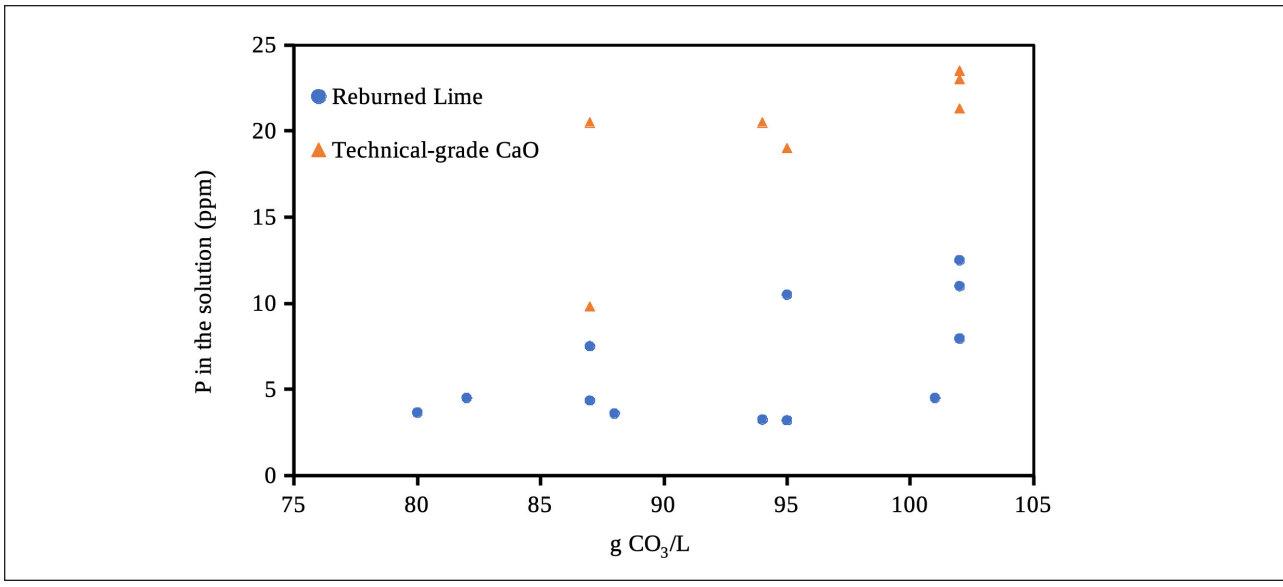
Ulmgren and Rådeström [10] showed that the final concentration of phosphate in white liquor is a function of lime addition and green/white liquor TTA. Because carbonate ions compete with phosphate ions for calcium, it was thought that the carbonate concentration would affect the final phosphorus concentration in white liquor after causticizing. Change in ionic strength could also impact the extent of reaction of phosphate with calcium due to the impact on the activity of dissolved ions. Both TTA and sulfidity were varied to give a range of carbonate concentrations and ionic strengths. For reburnt lime, the final concentration of phosphate in white liquor after slaking and causticizing at a liming ratio of 1.0 was essentially the same until an ionic strength of 5.6 M, then increased approximately linearly (**Fig. 2** and **Table I**). There was no clear correlation between the final phosphate concentration in the white liquor and carbonate concentration (**Fig. 3**).

TTA, g/L Na_2O	Sulfidity, % (TTA basis)	Initial P, ppm	CO_3, g/L	Ionic Strength
96	14	50	80	4.71
104	14	50	87	5.15
111	14	50	94	5.58
124	14	50	102	6.01
104	10	50	101	5.72
104	13	50	95	5.58
104	16	50	88	5.44
104	19	50	82	5.3
120	25	50	87	5.71
140	25	50	102	6.66
140	25	50	95	6.66
140	30	50	102	6.6

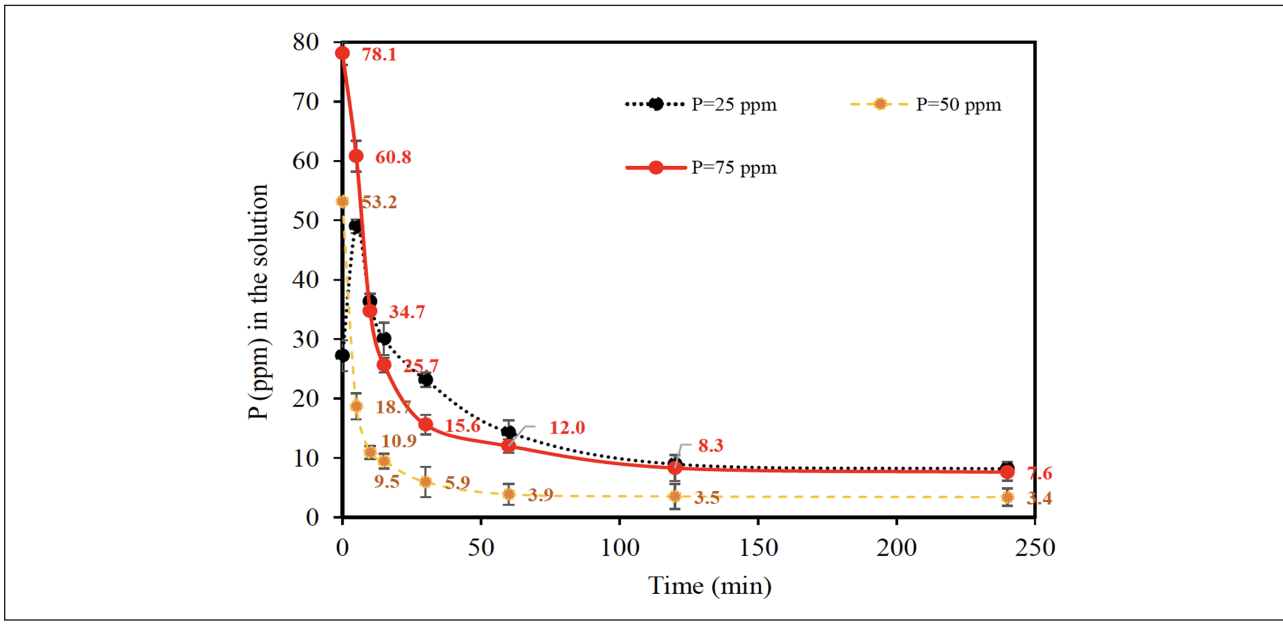
TTA: total titratable alkali; Na_2O: sodium oxide; P: phosphorus; CO_3: carbonate.

I. Experimental conditions for Fig. 2 and Fig. 3.

Some of the conditions run with reburnt lime were repeated with technical grade lime. The phosphate concentration at all ionic strengths was higher than the experiments with reburnt lime (Fig. 2). The same is true for all carbonate concentrations (Fig. 3). The primary differences between the technical grade lime and reburned lime are the reactivity and the difference of the presence of impuri-



3. Phosphorus (ppm P) in the white liquor as a function of carbonate (CO_3) concentration at a liming ratio of 1 for reburnt lime and technical grade lime (CaO). The initial P concentration in the green liquor was 50 ppm.

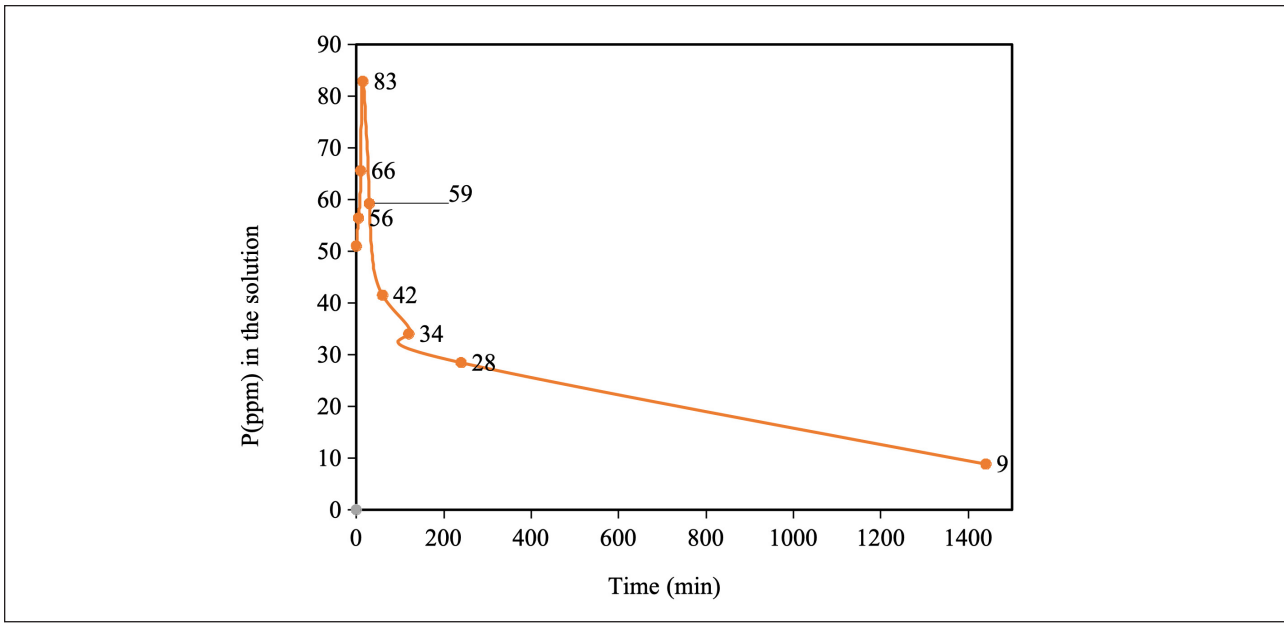


4. Phosphorus concentration (ppm P) in the liquor during 4 h reaction time with reburnt lime. Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.

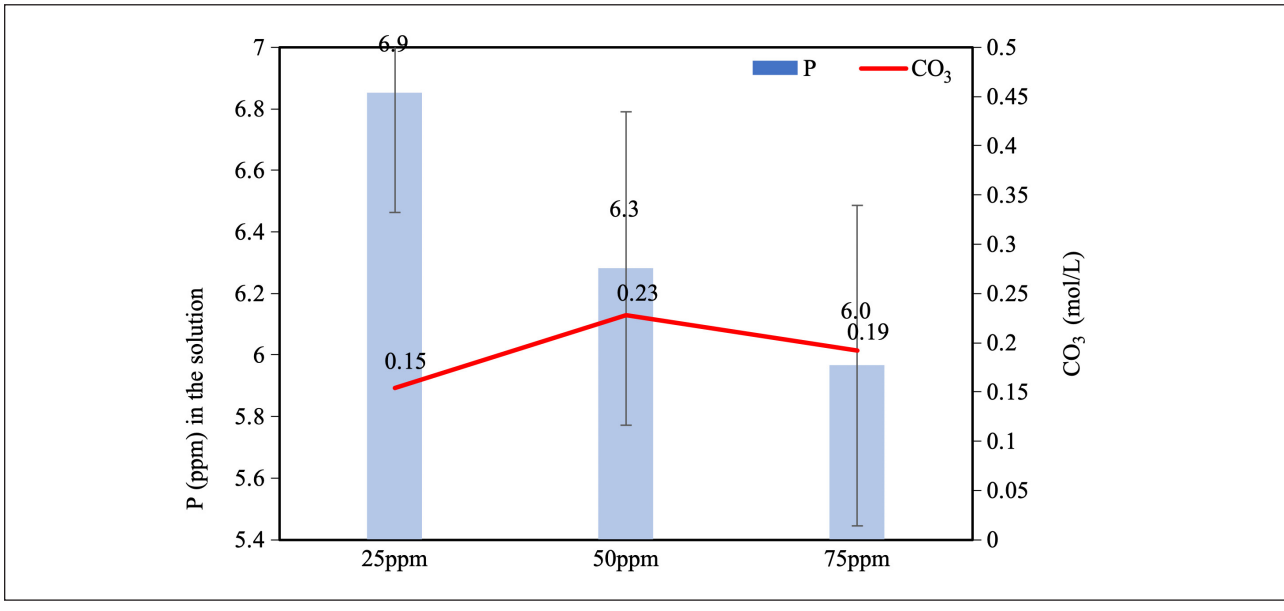
ties. The technical grade lime slakes faster, and we do see that the phosphorus concentration drops faster with the technical grade lime. This is consistent with the idea that $Ca(OH)_2$ reacts with phosphate, forming rhenanite. However, this does not explain why the final phosphorus concentration in the white liquor is higher for the technical grade lime than with the reburned lime.

The effect of phosphorus concentration in the green liquor on the final concentration of phosphorus in the white liquor was explored by slaking and causticizing a green liquor with TTA of 111 Na_2O g/L and sulfidity of 14 ± 1% (TTA basis), along with different initial phosphorus concentrations. For reburnt lime, a steady level of phosphorus in the white liquor was reached after about 2 h (**Fig. 4**). The final concentration achieved after 4 h was similar, regardless of the initial phosphorus concentration in the green liquor. Interestingly, for the GL with an initial concentration of 25 ppm, the phosphorus concentration increased after 5 min reaction time, and then it started to decrease. About 12% of lime's phosphorus is dissolved in the liquor before reprecipitation is seen.

Experiments were repeated with a green liquor con-



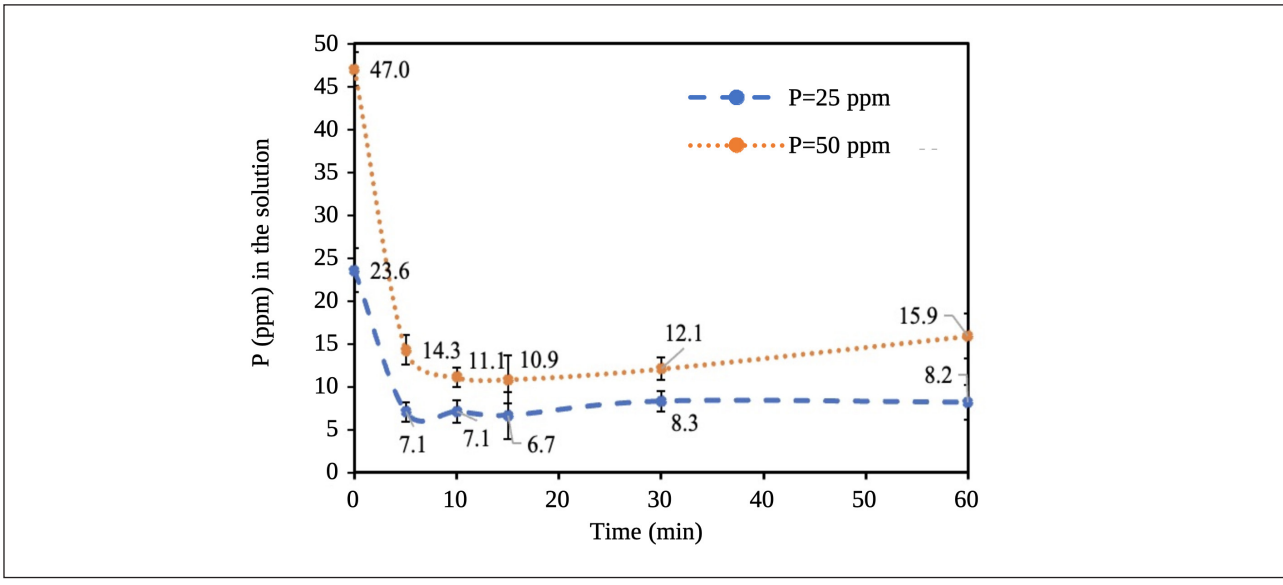
5. Phosphorus concentration (ppm P) in the liquor during 24 h reaction time for reburnt lime, with TTA = 140 g/L sodium oxide (Na_2O) and sulfidity 30%.



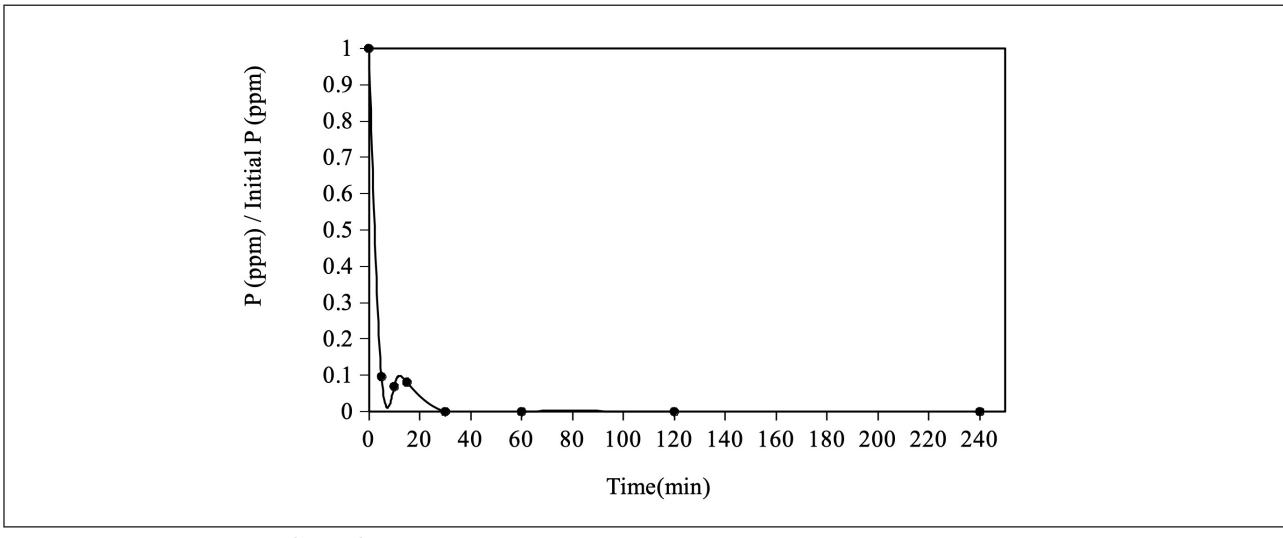
6. Concentration phosphorus (ppm P) and carbonate (CO_3) after 4 h of slaking/causticizing for green liquors with initial values of 25 ppm, 50 ppm, and 75 ppm. Liming ratio was 1.0.

taining a TTA of 140 Na_2O g/L and sulfidity of 30%, and an initial phosphorus concentration of 50 ppm. The solution had an initial carbonate concentration of 102 g carbonate ion (CO_3^{2-})/L and an ionic strength of 6.6 M. Phosphorus release was also seen with the 50 ppm phosphorus sample with the more concentrated green liquor (**Fig. 5**). The final concentration of phosphorus in the green liquor was 9 ppm after 24 h, which was very close to the range shown in **Fig. 6** after 4 h. This shows that even though there is a competition within the causticizing reactions between the $Ca(OH)_2$ and carbonate vs. $Ca(OH)_2$ and phosphate, if there is enough time, phosphate can react with $Ca(OH)_2$. This was in agreement with the mass balance results of the previous work that showed the phosphorus concentration in clarified green liquor and white liquor after the slaker were close, but the concentration of phosphorus in the white liquor after the last white liquor clarifier was lower [2].

At the lower green liquor phosphorus concentration, phosphorus can be transferred from the lime into the liquor initially, presumably due to the formation of $CaCO_3$ from the rhenanite. As causticizing continues, the carbonate con-



7. Phosphorus concentration (ppm P) in the liquor during 1 h reaction time for technical grade lime (CaO). Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.



8. Phosphorus concentration (ppm P) in the liquor for 4 h reaction time. Pre-slaked reburnt lime was added to green liquor, with TTA = 111 g/L sodium oxide (Na_2O), sulfidity = 14%, and P = 25 ± 3 ppm.

centration drops and phosphorus reacts with calcium to form rhenanite. The proposed reactions are:

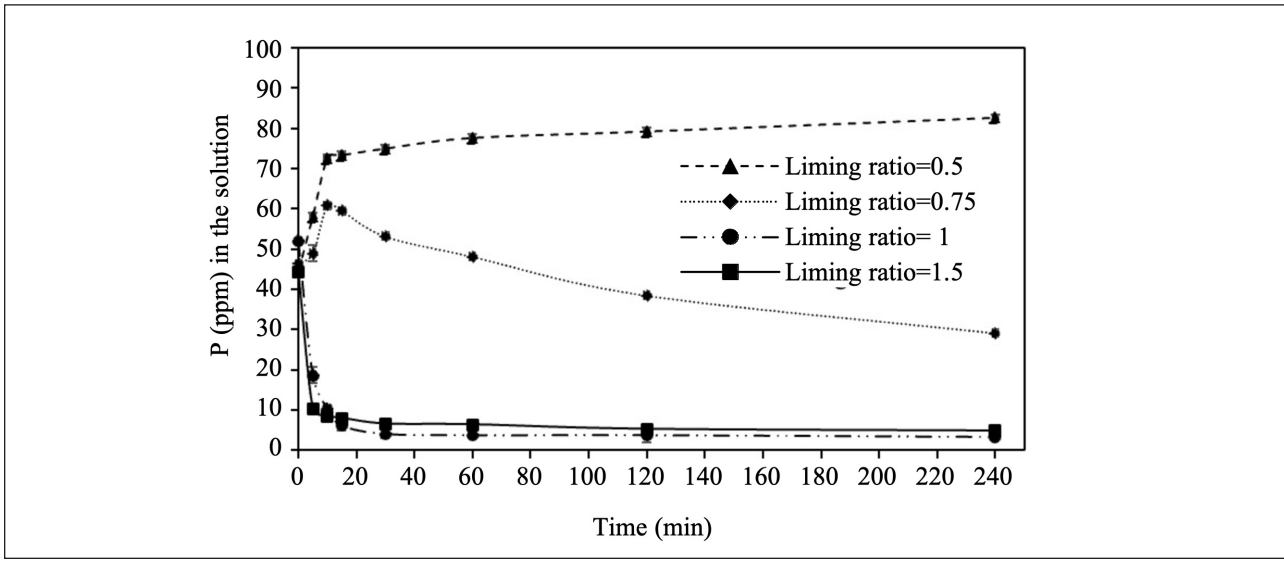
$$Ca(OH)_{2(s)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)} + 2OH^-{}_{(aq)} \quad (1)$$

$$Ca(OH)_{2\,(s)} + Na^+{}_{(aq)} + PO_4^{3-}{}_{(aq)} \rightarrow NaCaPO_{4(s)} + 2OH^- \quad (2)$$

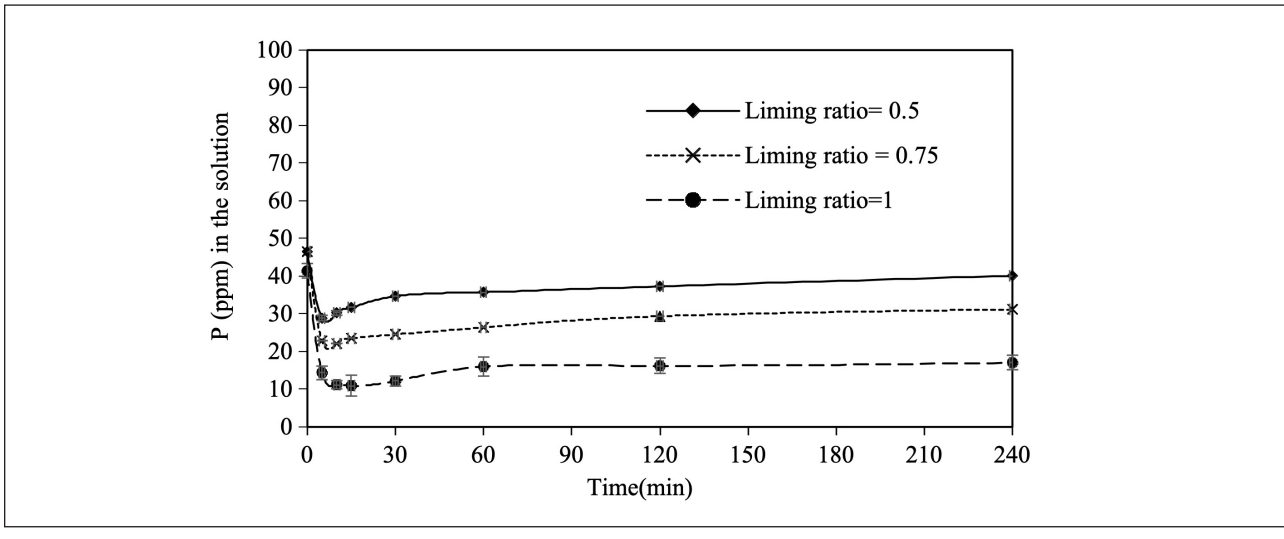
$$NaCaPO_{4(s)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons CaCO_{3(s)} + Na^+{}_{(aq)} + PO_4^{3-}{}_{(aq)} \quad (3)$$

The 25 ± 3ppm and 75 ± 3 ppm cases ended up at the same level after 4 h (Fig. 4). However, the final concentration of phosphorus in the 50-ppm case is slightly lower. In order to determine if the difference is repeatable, as a function of variability of the lime, the 4-h experiment was carried out five times for all three cases, and the final solution was titrated with 1 N HCl to find the final carbonate and hydroxide concentrations of the solutions. For all three cases, the final concentration of phosporus in the white liquor after 4 h was within 5–7 ppm, and since the error bars overlapped, this shows the values were not significantly different. The reason for why the final values are a little different is likely due to the slight variability of the lime, as shown in Fig. 6. The final carbonate concentrations are approximately the same, indicating that the extent of causticizing is about the same in all cases. These carbonate levels translate to a final causticity of 80%–82% for the three cases, which is consistent with the measured lime availability.

For technical grade CaO, most of the phosphorus pickup occurs in the first 5 min, and an approximately steady level of phosphorus is achieved in 10 min (**Fig. 7**). The differ-



9. Phosphorus concentration (ppm P) in the solution at different liming ratios for reburnt lime. The TTA was 111 g Na_2O/L, and the sulfidity was 14% on a TTA basis.



10. Phosphorus concentration (ppm P) in the solution at different liming ratios for lime (CaO). The TTA was 111 g Na_2O/L, and the sulfidity was 14% on a TTA basis.

ence between the rate at which phosphorus is picked up by technical grade CaO compared to reburnt lime is likely due to the difference in slaking rate. Based on average values for phosphorus in the liquor vs. time, there may be a slight dissolution of phosphorus in the 50 ppm run after 10 min, though the standard deviation of five runs was higher at 60 min than 30 min. This may simply be due to variability in the phosphorus reactions with lime in slaking and causticizing.

The results shown in Fig. 4 and Fig. 5 indicate that it is possible for the phosphorus to be solubilized within the first 5 min of the slaking/causticizing reaction, and the concentrations of both CO_3 and phosphorus in the green liquor will affect whether this occurs or not. The results with technical grade CaO indicate that the rate of phosphorus uptake may be related to the reactivity of the lime and rate of slaking. To separate slaking from causticizing reactions, reburnt lime was pre-slaked in water and then added to green liquor. The results tend to indicate that, in this case, reburnt lime behaves like CaO and most of the green liquor's phosphorus is picked up by the lime during the first 5 min (**Fig. 8**). This suggests that phosphate reacts with $Ca(OH)_2$ in the formation of rhenanite and that the rate of slaking is likely the primary factor in the rate of uptake of phosphate in slaking and causticizing. To investigate if phosphorus is released during slaking in water, one separate slaking experiment was conducted by adding reburnt lime to deionized water and slaking it for 2 h without carbonate ions present in the solution. There was no phosphorus detected in the solution.

To study the effect of liming ratio on phosphorus pickup by the lime, both technical grade CaO and reburnt lime were added to green liquor with a TTA of 111 Na_2O g/L, sulfidity of 14 ± 1% (TTA basis), and P = 50 ± 3ppm were slaked and causticized at different liming ratios (0.5, 0.75, 1, 1.5) (**Figs. 9–10**). Under these conditions, there is dissolution of phosphorus from the reburnt lime at a liming ratio of 0.5 and 0.75, with some reprecipitation at a liming ratio of 0.75. These results are generally consistent with the findings of Ulmgren and Rådeström [10].

It was expected that increased lime addition would result in increased phosphorus pickup, because the carbonate ions compete with phosphate for calcium ions. The results show that for technical grade CaO, as the liming ratio increased, more phosphorus was picked up from the liquor by the lime and the system. The initial pick up of phosphorus occurred within 10 min, but then a very small amount of phosphorus was released over time (Fig. 10), which is consistent with earlier figures for technical grade lime.

CONCLUSION

For reburnt lime, ionic strength can impact uptake of phosphorus by lime above an ionic strength of ~5.6 M. The carbonate concentration does not have a clear impact beyond impacting ionic strength. The practical implication is that slightly less phosphorus in the green liquor will react with reburnt lime if the TTA is closer to 140 g Na_2O/L compared to 120 g Na_2O/L. Additionally, if the concentration of carbonate is high and the concentration of phosphorus is low in the green liquor, there can be initial dissolution of phosphorus from the lime prior to reaction of the calcium hydroxide with phosphate in the green liquor. The reactivity of the reburnt lime will affect the rate of phosphorus reaction with the lime. This is because the reaction of phosphorus uptake does appear to be with the slaked lime. If there is enough time, at a liming ratio of 1, the final concentration of phosphorus in the white liquor will likely be in the range of 5–10 ppm, regardless of initial phosphorus concentration of the green liquor. Finally, overliming will have only a slight impact on phosphorus uptake. The results with pre-slaked lime seem to clearly indicate that what limits the rate as phosphorus in liquor reacts with lime during slaking and causticizing is tied to the rate at which slaking occurs. However, there does appear to be another feature of reburned lime that affects the final concentration of phosphorus in the white liquor after slaking and causticizing. It would be interesting to repeat these experiments with different mill limes that have different histories and compositions to see if there are quantifiable differences. Alternatively, technical grade lime could be mixed with impurities or sintered to varying degrees to identify the root cause of these differences. **TJ**

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ABOUT THE AUTHORS

Phosphorus is not only a deadload in the lime cycle, but an element that has potential value for recovery long term. Our interest in this work was to better understand the factors that control the distribution of phosphorus between the solid and liquid phase in slaking and causticizing. This work complements earlier studies by Ulmgren and Rådeström, providing additional insight into the reactions phosphorus undergoes during slaking and causticizing and showing that there are some differences in behavior between analytical grade lime and reburnt lime.

The initial challenge in this study was that both slaking and causticizing occur when lime is added to black liquor, and there can thus be competing reactions between phosphate and carbonate. The most interesting finding was that not only the rate of reaction between phosphate in the green liquor and the solid was significantly different, but that more phosphorus reacted with the reburned lime than the analytical grade lime.

This study will contribute to the broader non-process elements project in our research group. With this study, mills can see that slaking and causticizing conditions have little influence on the extent to which phosphorus reacts with lime. From this perspective, the accumulation of phosphorus in lime is predictable if the mill knows the input of phosphorus to the recovery cycle.

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