Factors Affecting Phosphorus Up-take/Dissolution during Slaking and Causticizing

Maryam Sadegh Mousavi[1], Nikolai DeMartini

Department of Chemical Engineering, University of Toronto, 200 College Street, Toronto, ON, Canada, M5S3E5

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 phosphorous 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 P and only mildly dependent on the carbonate concentration in the green liquor. There does 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.

Introduction

Phosphorous, a non-process element in kraft pulp mills, enters the digester with the wood and white liquor [1-3]. Essentially all of the P exists with the black liquor to evaporation [2]. The amount of phosphorous entering with the wood depends on the wood species, harvest season, and geographical location [4]. Furthermore, different parts of a tree have different concentrations of P, with the concentration in bark being higher than in the stem wood on a dry mass basis [4]. Thus, poor debarking can result in an increase of phosphorous into digestion. Phosphorous is carried through the evaporators with the black liquor to the recovery boiler and the majority of the P in the black liquor exits with the smelt and is entrained with the green liquor. It is this P that reacts with the lime in the slaking and causticizing process. Other sources of phosphorous in the recovery cycle can be make-up lime, process water, bio-sludge (10-500mg/kg d.b.) and biofuels (4-191

---

[1] E-mail: Maryam.Mousavi@utoronto.ca

mg/kg d.b. with wood and 428-1260 mg/kg d.b. with bark) if burned in the lime kiln [5-8].The phosphorous 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 P in the Nordic mills could be the combustion of biosludge with the black liquor in some Nordic mills.

In the recausticizing process, phosphorous 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 [2,9]. Mills need to purge some lime mud and use fresh lime to maintain their desired lime availability and prevent the formation of deadload in the lime cycle [12]. 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 Na^+ and CO_3^{2-} [10,13]. Going forward, we will refer to the phosphorous containing compound in lime and lime mud as rhenanite, based on our earlier findings.

Ulmgren and Rådeström [9] 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 ℃ and 90 ℃ . The initial phosphorus 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 CaO, with a few conducted with reburnt lime (lime availability = 84%). Based on the results of their study, phosphorus pick-up 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 [9]. They showed that the time needed to reach equilibrium for Ca ions when it was added as $CaCO_3$ or $Ca(OH)_2$ was a few hours. However, the time that took for PO_4 to reach equilibrium in green and white liquors containing excess amount of P were 30 and 60 days, respectively. The phosphate ion concentration in the white liquor after 3hr. and 60 days were 13.95 and 5.58 ppm [9].In another work done by Ulmgren and Rådeström [13], 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 PO_4 concentration in green and white liquor. They showed that the time to reach a steady state PO_4 concentration in green and white liquors were between 4-20 weeks at different Ca/P ratios. The steady state solubility of PO_4 in green and white liquors at 90°C were 95 ppm and 3.72 ppm, respectively [13].

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 P uptake by lime was investigated by pre-slaking the lime, and, in some experiments, followed by addition to green liquor for causticizing reaction 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 TTAs, sulfidities and phosphorus concentrations were prepared using Na_2CO_3 (ACS grade, anhydrous, 99.5%), Na_2S (technical grade), and Na_3PO_4 (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 1N HCl.

A 2kg sample of reburnt lime with initial lime availability of (92%±2) was obtained from a Canadian mill and was calcined at 950 □ for 2 hours prior to each experiment. Technical-grade CaO was also heated up to 550 □ prior to the experiments to ensure there is no $Ca(OH)_2$ present. All the slaking/causticizing reactions were done at (95 ± 2□) in a water bath which held a 250 ml fluoropolymer (PFA) bottle with a magnetic stir. 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 high concentration of sodium ions, samples were diluted with 5% nitric acid prior to being analyzed by ICP-OES (213.618 nm). The average concentration variability for phosphorus obtained from ICP-OES measurements for the initial green liquor solutions was ±3ppm 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 hours to make sure that a steady concentration is reached within four hours.

Results and Discussion

A series of experiments were conducted for eight hours to see when the system reaches equilibrium. These experiments were done at two different TTAs (104 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 eight hours. After two hours, the concentration of phosphorus in the liquor became constant for these conditions (Figure 1).

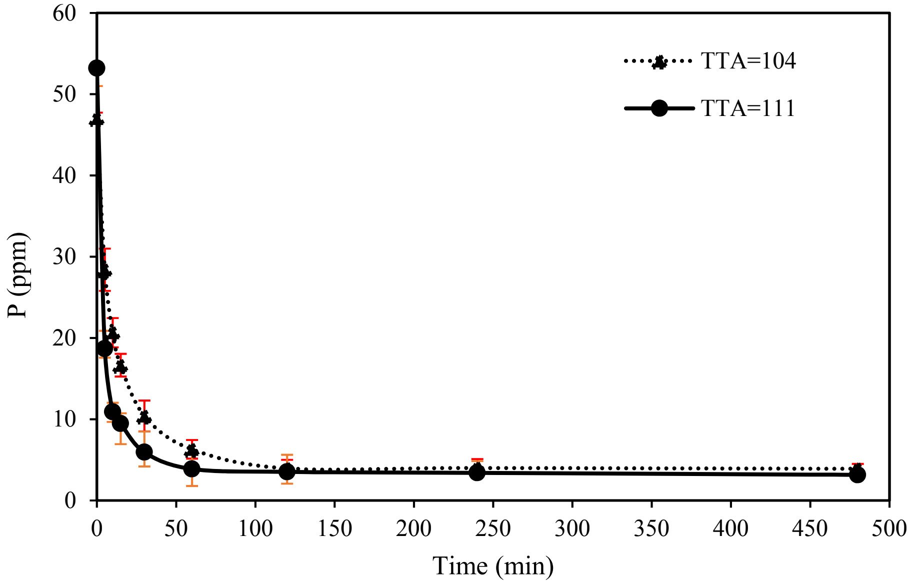

Figure 1. Phosphorus concentration in the liquor with low TTAs (111, 104) during eight hours of reaction time. Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.

Ulmgren and Rådeström [9]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 phosphorous 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 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 (Figure 2 and Appendix). There was no clear correlation between the final phosphate concentration in the white liquor and carbonate concentration, Figure 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 (Figure 2). The same is true for all carbonate concentrations (not shown in Figure 3). This might be due to the difference between the slaking rate/reactivity of reburnt lime and technical-grade CaO because technical-grade CaO slakes faster. Therefore, technical-grade CaO quickly slakes and reacts with sodium carbonate as opposed to with phosphate, resulting less phosphorus is picked up. The other difference between technical-grade CaO and reburnt lime is in the availability of their active sites. Reburnt lime has fewer active sites available due to the presence of impurities such as MgO. Therefore, it is less reactive compared to technical-grade CaO.

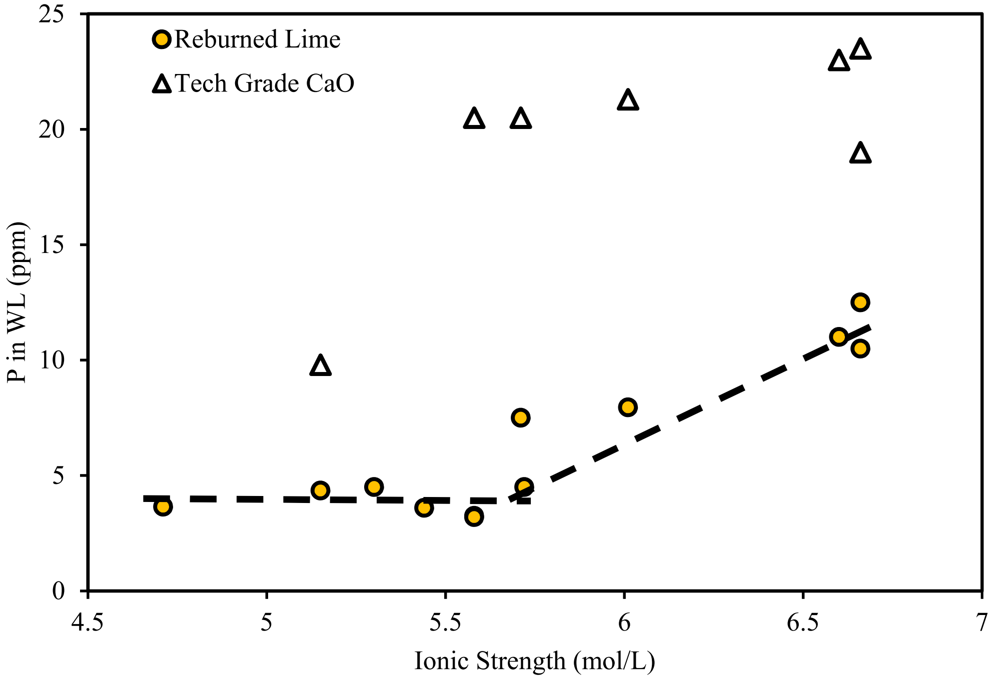

Figure 2. P in the white liquor (ppm P) as a function of ionic strength at a liming ratio of 1 for reburnt lime and technical grade CaO. The initial P concentration in the green liquor was 50 ppm.

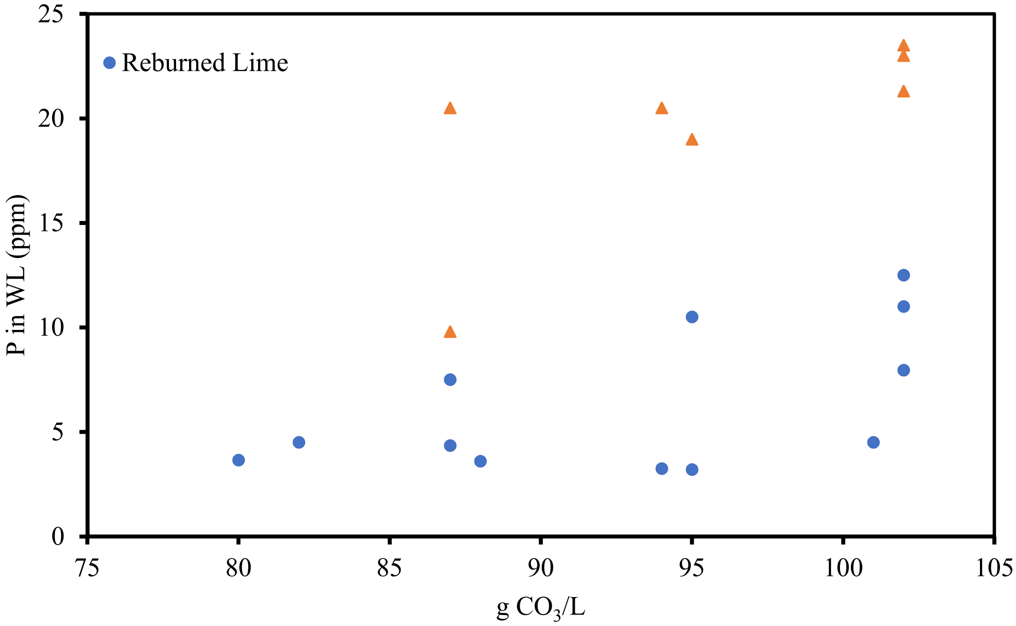

Figure 3. P in the white liquor (ppm P) as a function of carbonate concentration at a liming ratio of 1 for reburnt lime and technical grade CaO. The initial P concentration in the green liquor was 50 ppm.

The effect of phosphorus concentration in the green liquor on final WL phosphorous 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 P in the white liquor was reached after about 2hrs. (Figure 4). The final concentration achieved after 4h was similar regardless of the initial P 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.

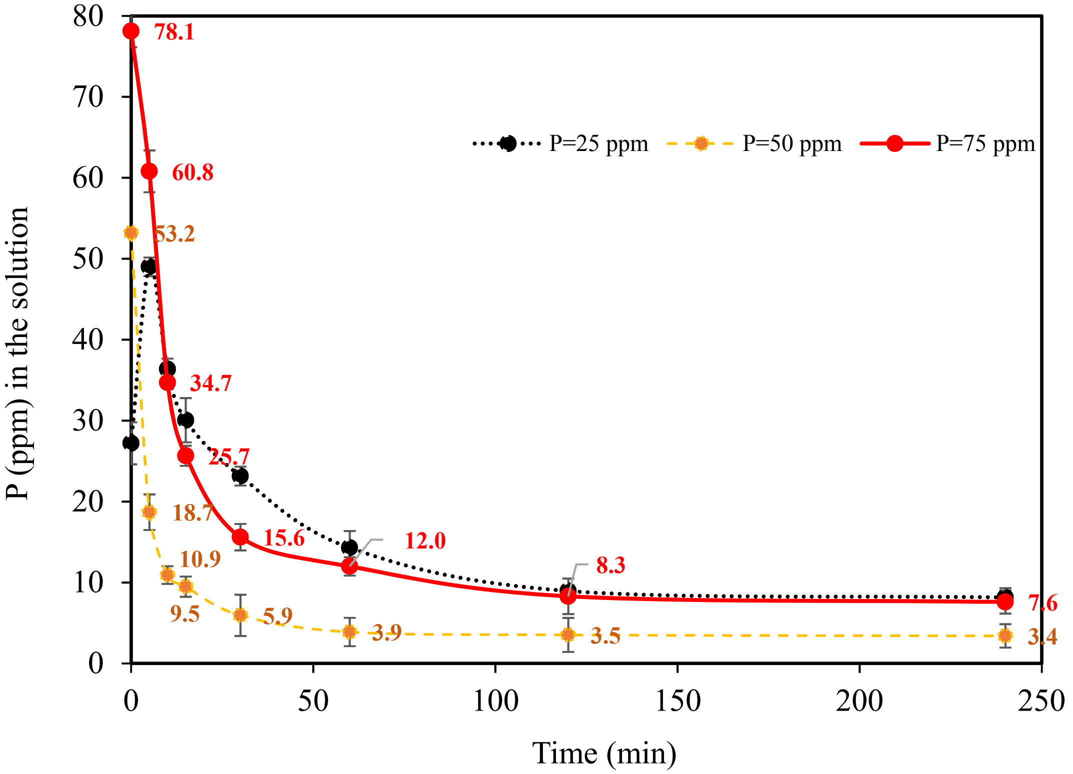

Figure 4. Phosphorus concentration in the liquor during 4h reaction time with reburnt lime. Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.

Experiments were repeated with a green liquor containing a of TTA 140 Na_2O g/L and sulfidity of 30%, and an initial phosphate concentration of 50 ppm. The solution had an initial carbonate concentration of 102 g CO_3/L, and an ionic strength of 6.6 M. Phosphorus release was also seen with the 50ppm phosphorus sample, with the more concentrated green liquor (Figure 5). The final concentration of phosphorus in the green liquor was 9 ppm after 24 hours which was very close to the range showed in Figure 6, after 4 hours. This shows that even though there is a competition within the causticizing reactions, between the $Ca(OH)_2$ and carbonate versus $Ca(OH)_2$ and rhenanite, if there is enough time, rhenanite 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].

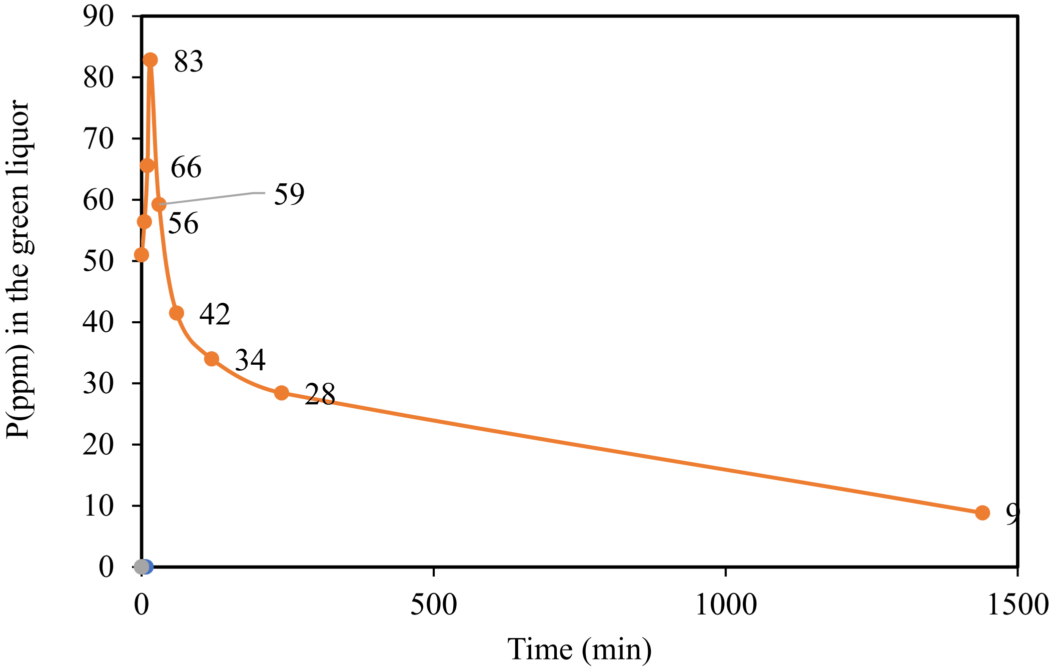

Figure 5. Phosphorus concentration in the liquor during 24hr. reaction time for reburnt lime. TTA=140 g/L Na_2O and sulfidity 30%.

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 concentration drops and phosphorous reacts with calcium to form rhenanite. The proposed reactions are:

$$Ca(OH)_{2(s)} + CO_3^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)} + 2OH^-{}_{(aq)} \qquad /1/$$

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

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

The 25 ± 3ppm and 75 ± 3 ppm cases ended up at the same level after four hours (Figure 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 four-hour experiment was carried out five times for all three cases and the final solution was titrated with 1N HCl to find the final carbonate and hydroxide concentrations of the solutions. For all three cases, the final concentration after four hours was within a 5-7ppm and since the error bars overlapped, this shows the values were not significantly different. Likely the reason for why the final values is a little different is due to the slight variability of the lime, as shown in Figure 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.

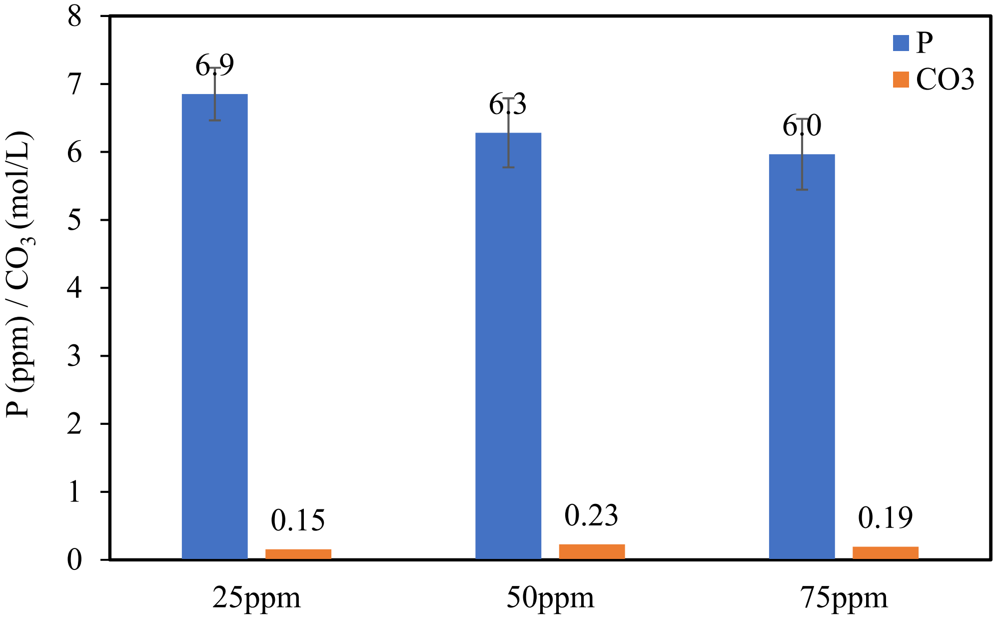

Figure 6. Concentration of phosphorus and carbonate after 4 hours of slaking/causticizing for green liquors with initial values of 25 ppm, 50 ppm and 75 ppm. Liming ratio of 1.0.

For technical-grade CaO, most of the phosphorous pick-up occurs in the first 5 minutes and an approximately steady level of P is achieved in 10 min (Figure 7). The difference between the rate at which P 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 P in the liquor versus time, there may be a slight dissolution of P 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 P reactions with lime in slaking and causticizing.

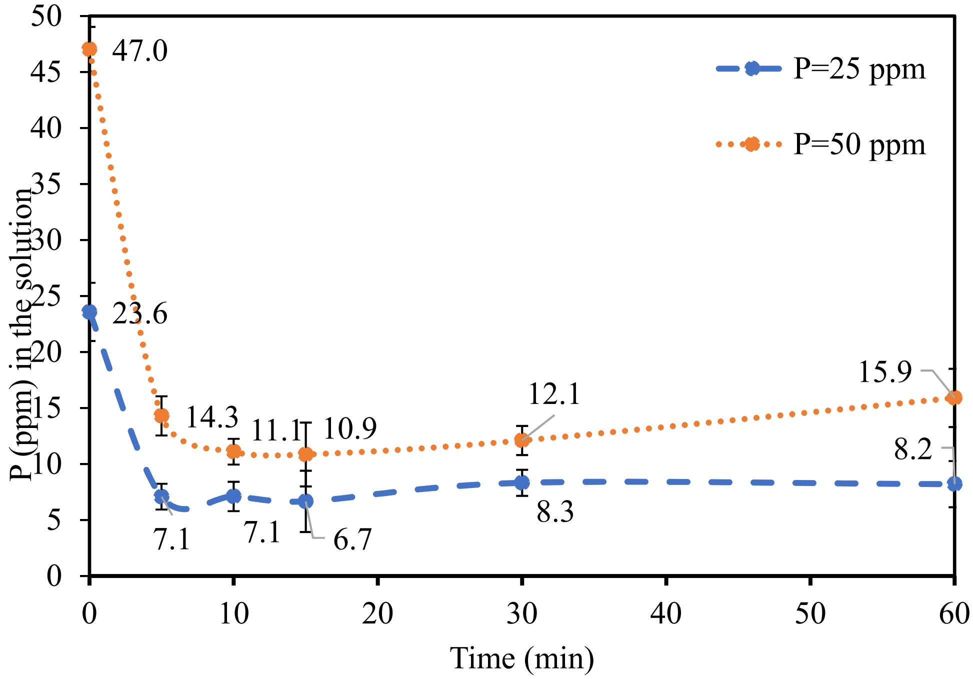

Figure 7. Phosphorus concentration in the liquor during 1h reaction time for technical-grade CaO. Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.

The results shown in Figures 4 and 5 indicate that it is possible for the phosphorus to be solubilized within the first five minutes of the slaking/causticizing reaction and the concentrations of both CO_3 and P in the green liquor will affect whether this occurs or not. The results with technical grade CaO indicate that the rate of P 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 was 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. (Figure 8). This suggests that phosphate reacts with $Ca(OH)_2$ in the formation of rhenanite and that the rate of slaking is the likely the primary factor in the rate of uptake of phosphate in slaking and causticizing. To investigate if phosphorous is released during slaking in water, one separate slaking experiment was conducted by adding reburnt lime to deionized water and slaking it for two hours without carbonate ions present in the solution. The results showed that there was no phosphorus in the solution.

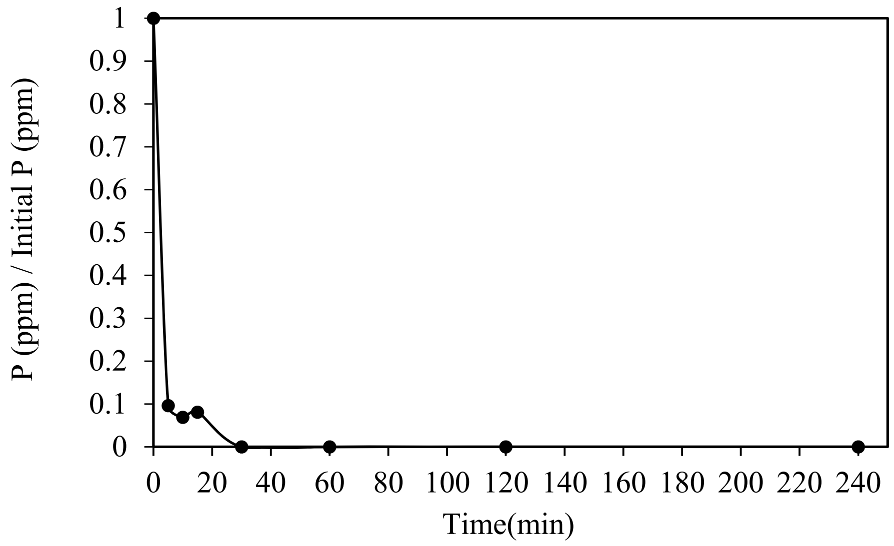

Figure 8. Phosphorus concentration in the liquor for 4 hours reaction time. Pre-slaked reburnt lime was added to green liquor (TTA=111 g/L Na_2O, sulfidity = 14%, P= 25±3 ppm)

To study the effect of liming ratio on phosphorus pick-up 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) (Figures 9 and 10). Under these conditions, there is dissolution of P 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 [9].

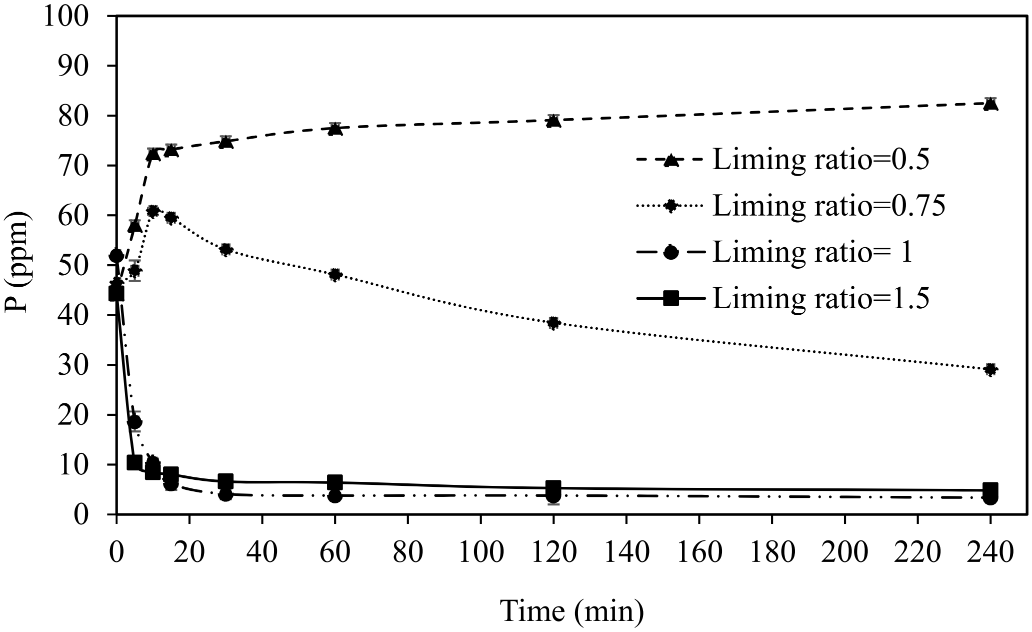

Figure 9. Phosphorus concentration in the solution at different liming ratios for reburnt lime. initial carbonate concentration= 94 g/L

It was expected that increased lime addition would result in increased phosphorus pick-up because the carbonate ions compete with phosphate for calcium ions. The results shown, 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 P occurred within 10 min, but then very small amount of phosphorus was released over time (Figure 10) which is consistent with earlier figures for technical grade lime.

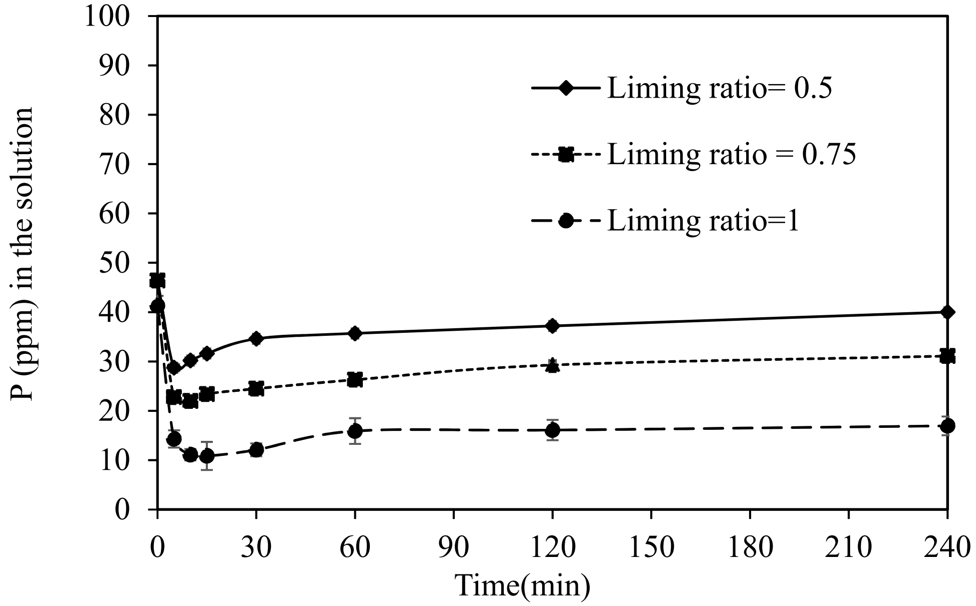

Figure 10. Phosphorus concentration in the solution at different liming ratios for CaO (initial carbonate concentration= 94 g/L)

Conclusion

For reburnt lime, ionic strength can impact uptake of P by lime above an ionic strength of ~5.6M. The carbonate concentration does not have a clear impact beyond impacting ionic strength. The practical implication is that slightly less P 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 P is low in the green liquor, there can be initial dissolution of P 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 P reaction with the lime. This is because the reaction of P uptake does appear to be with the slaked lime. If there is enough time, at a liming ratio of 1, the final concentration of P in the white liquor will likely be in the range of 5-10 ppm regardless of initial phosphorus concentration of the green liquor. Finally, over-liming will have only a slight impact on P uptake.

References

[1] H. Magnusson, K. Mork and B. Warnqvist, "Non-Process Chemical Elements in the Kraft Recovery System," in *TAPPI ATCP Pulping Conference*, Seattle, 1979.

[2] M.Mousavi,N. DeMartini, "Fate of phosphorus in the recovery cycle of the kraft pulping process," *TAPPI J.,* vol. 19, no. 3, pp. 139-148, 2020.

[3] T. Fossum, N. Hartler and J. Lihert, "The Inorganic Content of Wood," *Svensk Papperstidn,* vol. 75, no. 8, p. 305, 1972.

[4] B. Jonsson, Perrzestdl and L. Hong-Kou, "Analysis of Content of Trace Elements in Tree Cores from Spruce by Means of Pixe," Swedish University of Agricultural Science , 1990.

[5] A.Asemaninejada,J.Arteagaa,G.Spiersa,P.Becketta, S.McGarryd, N.Mykytczuka,N.Basiliko, "Blended pulp mill, forest humus and mine residual material Technosols for T mine reclamation: A growth-chamber study to explore the role of physiochemical properties of substrates and microbial inoculation on plant growth," *Journal of Environmental Management* , vol. 228, pp. 93-102, 2018.

[6] J. Werkelin, B. Skrifvars, M. Zevenhoven, B. Holmbom, M. Hupa, "Chemical forms of ash-forming elments in woody biomass fuels," *Fuel,* vol. 89, pp. 481-493, 2010.

[7] A.Hyvonen, "The Effect of Non-Process Elements in Biosludge on the Recovery Cycles in Kraft Pulp Mills," MASc Thesis, University of Jyvaskyla, 2015.

[8] M. Bialik, A. Ahlroth and Mikael, "New Challenges Regarding Non-Process Elements in the Liquor and Lime Cycles," *TAPPI Journal,* vol. 14, pp. 421-429, 2015.

[9] P. Ulmgren and R. Rådeström, "The Build-up of Phosphorus in a Kraft Pulp Mill and the Precipitation of Calcium Phosphate from Green and White Liquors," *Journal of Pulp and Paper Science,* vol. 23, no. 2, pp. J52-J58, 1997.

[10] B.Mcguffie,K.Taylor, "Non-Process Element Mass Balance Improves Recaust and Lime Kiln Efficiency at Elk Falls Mill," in *in PAPTAC Parksville Conference and PACWEST Jasper Conference*, 2006.

[11] K.Karlemo, "Non-process elements in the recovery cycle of six Finish Kraft pulp mills," Abo Academy, Turko,Finland, 2019.

[12] B.Blackwell, "Dead Load Reduction in the Kraft Pulping Process: Memorandum 1: Causticizing," Environment Canada, 1984.

[13] P. Ulmgren and R. Rådeström, "The Composition of Calcium Phosphates Precipitated from Green and White Liquors," *Nordic Pulp and Papar Research Journal,* vol. 12, no. 3, pp. 167-174, 1997.

Appendix. Experimental Conditions for Figures 2 and 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