

Factors Affecting Phosphorus Uptake/Dissolution in Slaking/Causticizing

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About Phosphorus

- P can enter the mill with wood, biosludge and biofuels
- Phosphorus is known to decrease lime availability
- The main purge points are lime mud and lime kiln dust



Why phosphorus is important ?

P compounds

- Formation of non-reactive Ca-PO_4

Deadload in lime mud

- Increased energy and lime consumption

Lime availability

- P decreases lime availability

Biofuels

- Introduction of P with biofuels



Background

- Previous work showed the form of P in lime and lime mud is rhenanite (NaCaPO_4)
- There is a competition between PO_4^{3-} and CO_3^{2-} for calcium during slaking and causticizing



Objectives

To understand factors affecting P uptake during slaking and causticizing:

Effect of ionic strength :

- Change TTA (constant sulfidity)
- Change sulfidity (constant TTA)

Effect of P concentration :

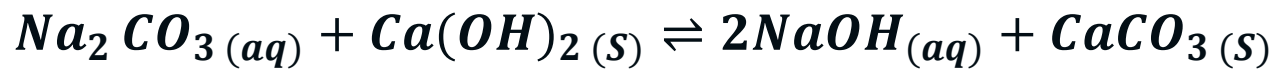
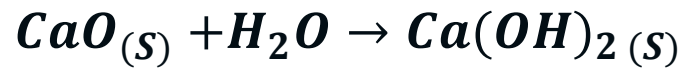
- Change the PO_4^{3-} concentration in green liquor

Effect of liming ratio

Comparison between the behavior of reburned lime and technical-grade CaO



Recausticizing Process



- **Lime Availability :**
The amount of CaO available for slaking

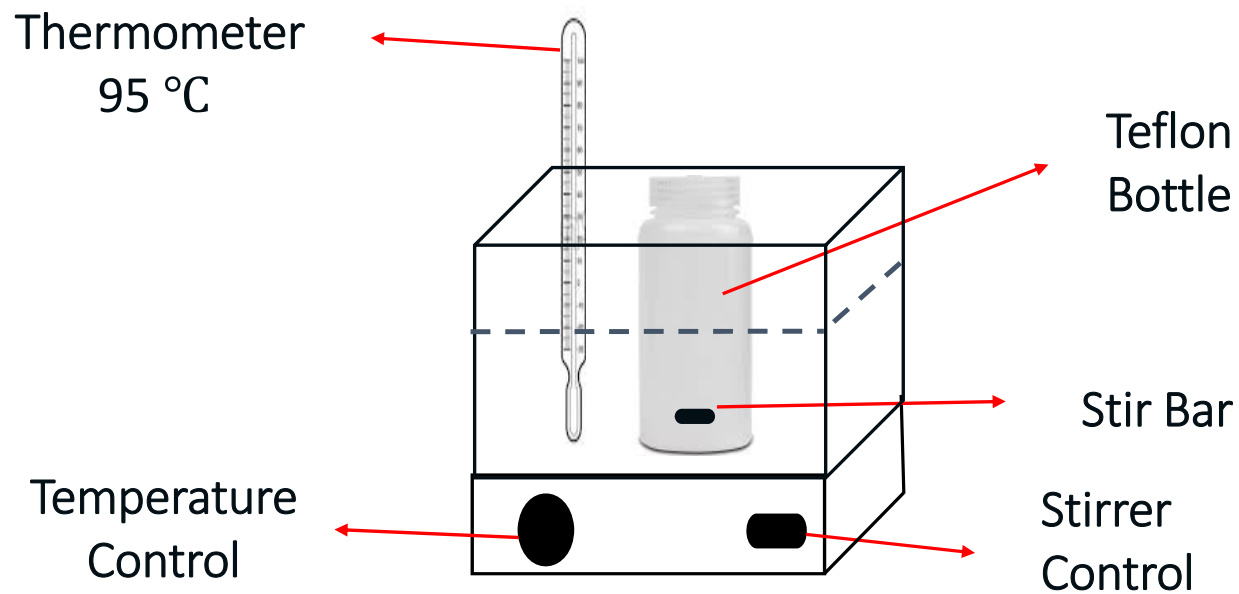
Lime



Courtesy of Valmet



Experimental Set-up



For all experiments, synthetic green liquor was made with Na_2CO_3 and Na_2S

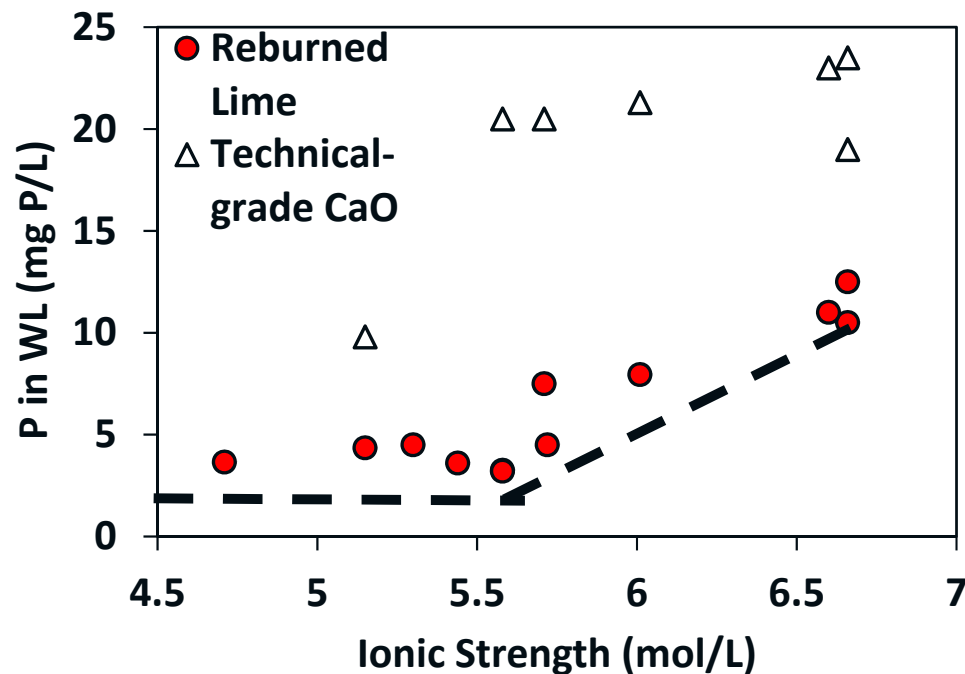


Experimental : Effect of Ionic Strength

Variable	
TTA	96-140 g/L Na ₂ O
Sulfidity	10—30 % (TTA basis)
P concentration	50 mg/L as Na ₃ PO ₄
Liming ratio	1 ± 0.1
Slaking and causticizing time	4 h
Lime type	Technical-grade CaO and reburnt lime



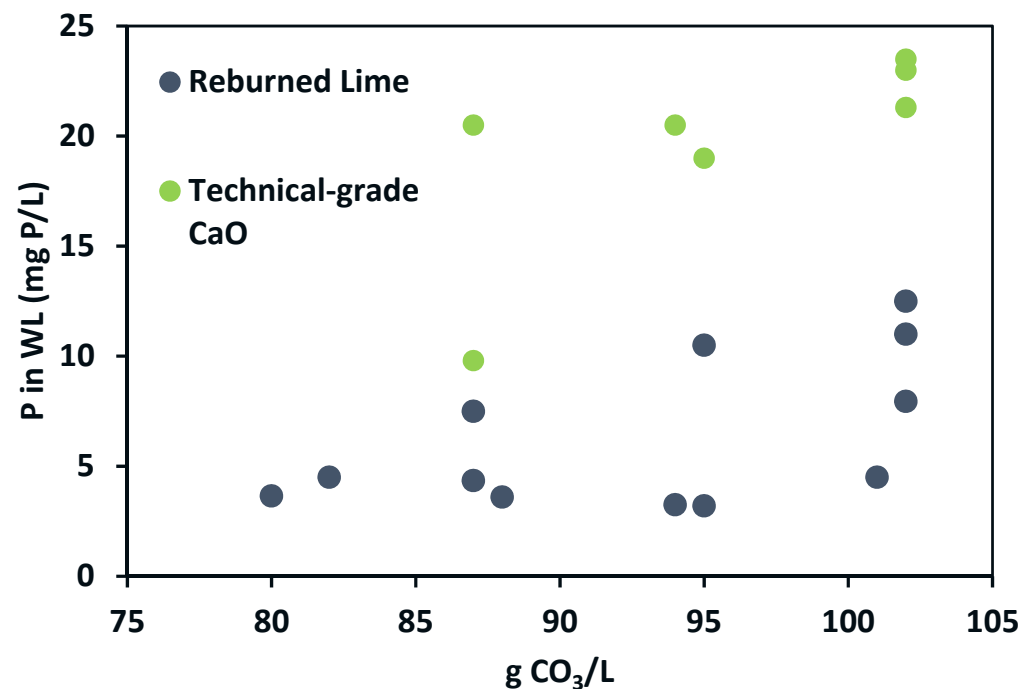
Effect of Ionic Strength



- P concentration in WL remains constant up to an ionic strength of 5.6 M. But increases linearly beyond this point.



Effect of CO_3 on the Final P Concentration in WL



- There was no clear correlation between the final phosphate concentration in the white liquor and carbonate concentration
- The P concentration at all ionic strengths was higher for Tech-grade CaO than for the reburned lime. Likely due to a difference in their reactivity

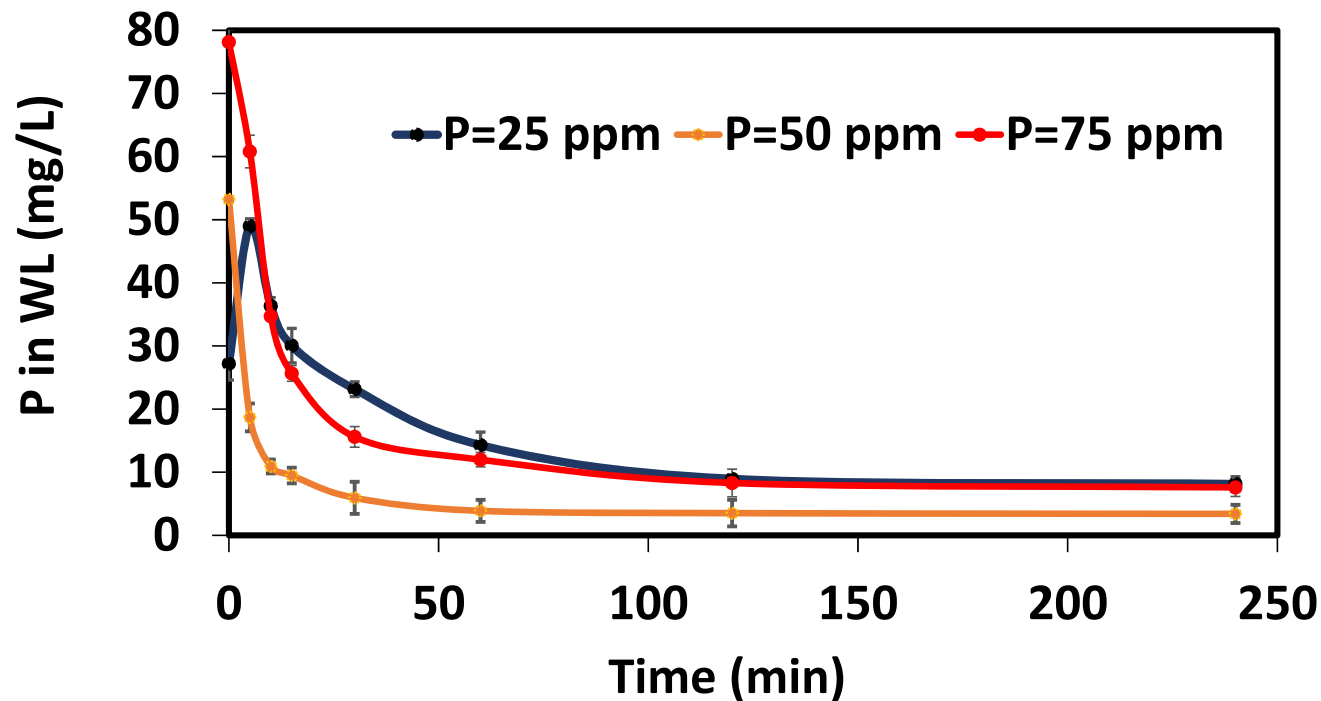


Experimental : Changing Green Liquor P Concentration

Variable	
TTA	111 g/L Na ₂ O
Sulfidity	14 % (TTA basis)
P concentration	25, 50 and 75 mg/L as Na ₃ PO ₄
Liming ratio	1 ± 0.1
Slaking and causticizing time	4 h
Lime type	Technical-grade CaO and reburnt lime



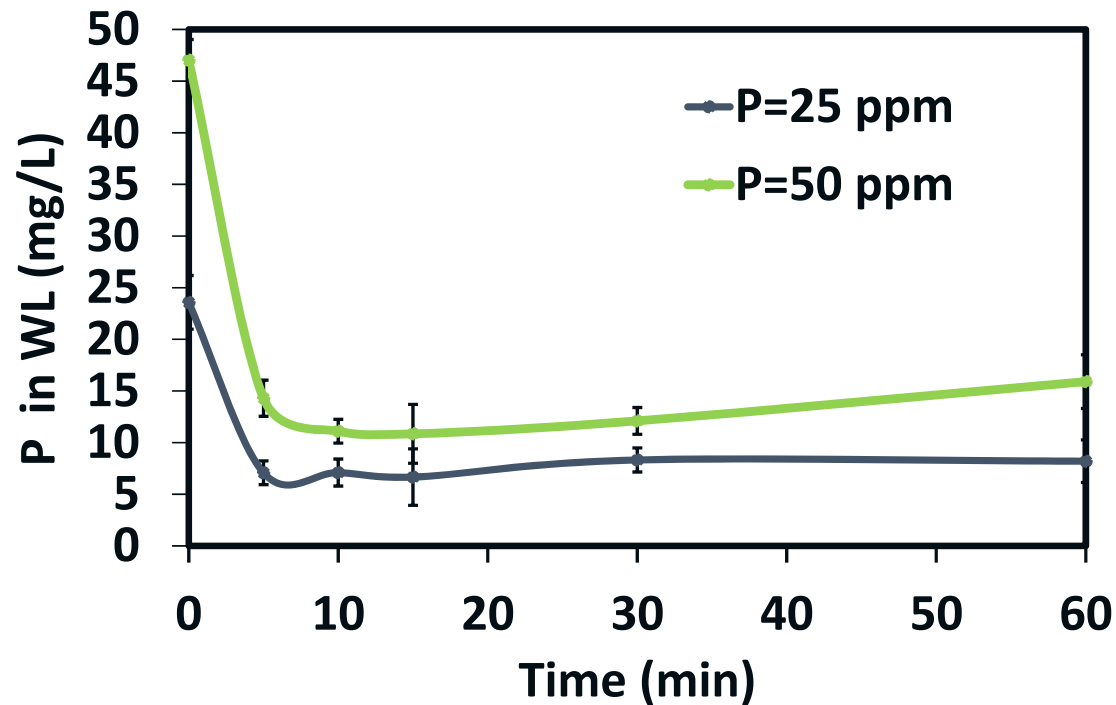
Effect of P Concentration on P Pick-up/Dissolution (Reburnt Lime)



Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.



Effect of P Concentration on P Pick-up/Dissolution (Technical-Grade CaO)



Error bars represent 1 standard deviation of at least 5 replicate analyses of the samples.



Proposed Dissolution Mechanism

- $\text{Ca(OH)}_{2(s)} + \text{CO}_3^{2-}(\text{aq}) \longrightarrow \text{CaCO}_{3(s)} + 2\text{OH}^-(\text{aq})$
- $\text{Ca(OH)}_{2(s)} + \text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \longrightarrow \text{NaCaPO}_{4(s)} + 2\text{OH}^-$
- $\text{NaCaPO}_{4(s)} + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{CaCO}_{3(s)} + \text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$



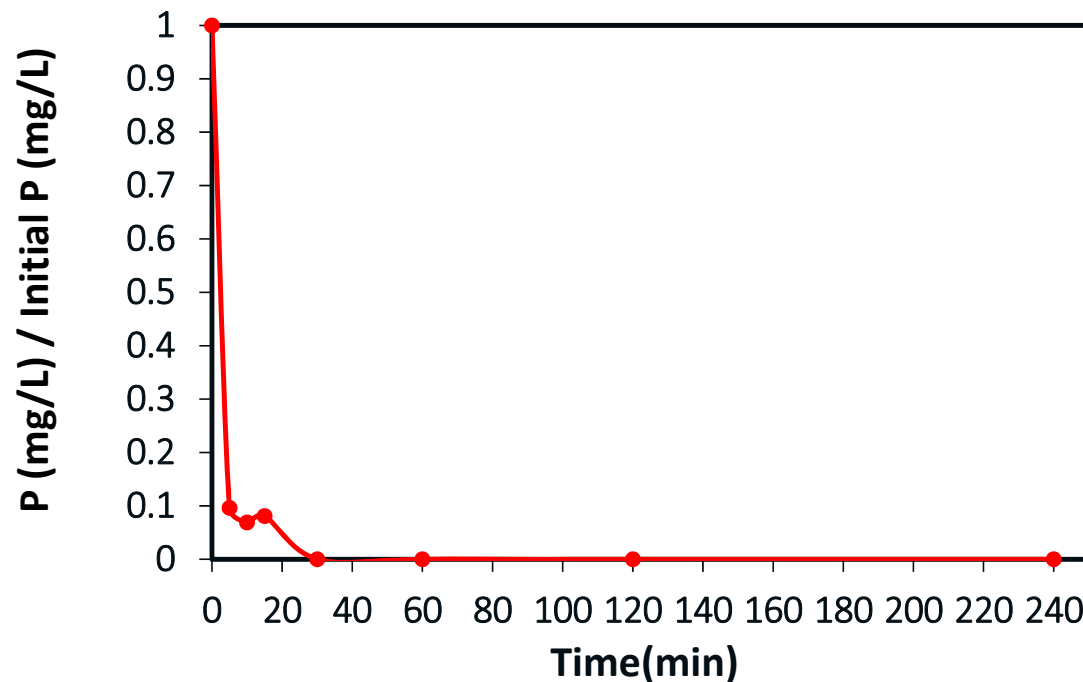
Separate Slaking and Causticizing Experiment

Reburnt lime was first slaked in water and then the slaked lime was added to Green liquor.

Variable	
TTA	111 g/L Na ₂ O
Sulfidity	14 % (TTA basis)
P concentration	25 mg/L as Na ₃ PO ₄
Liming ratio	1 ± 0.1
Slaking and causticizing time	4 h
Lime type	reburnt lime



Results: Separate Slaking & Causticizing Experiment



- Phosphate reacts with $\text{Ca}(\text{OH})_2$, resulting in the formation of rhenanite
- The rate of slaking is likely the primary factor influencing the rate of (P) uptake

Samples were taken after the pre-slaked lime was added to the green liquor

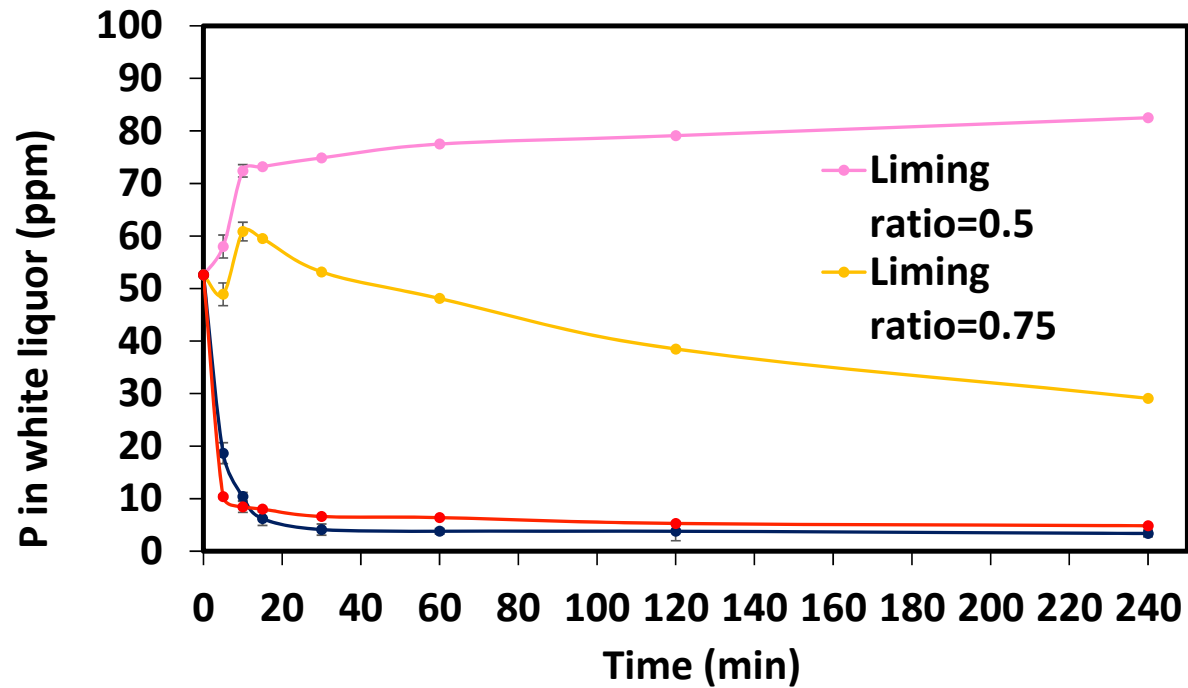


Experimental :Effect of Liming Ratio

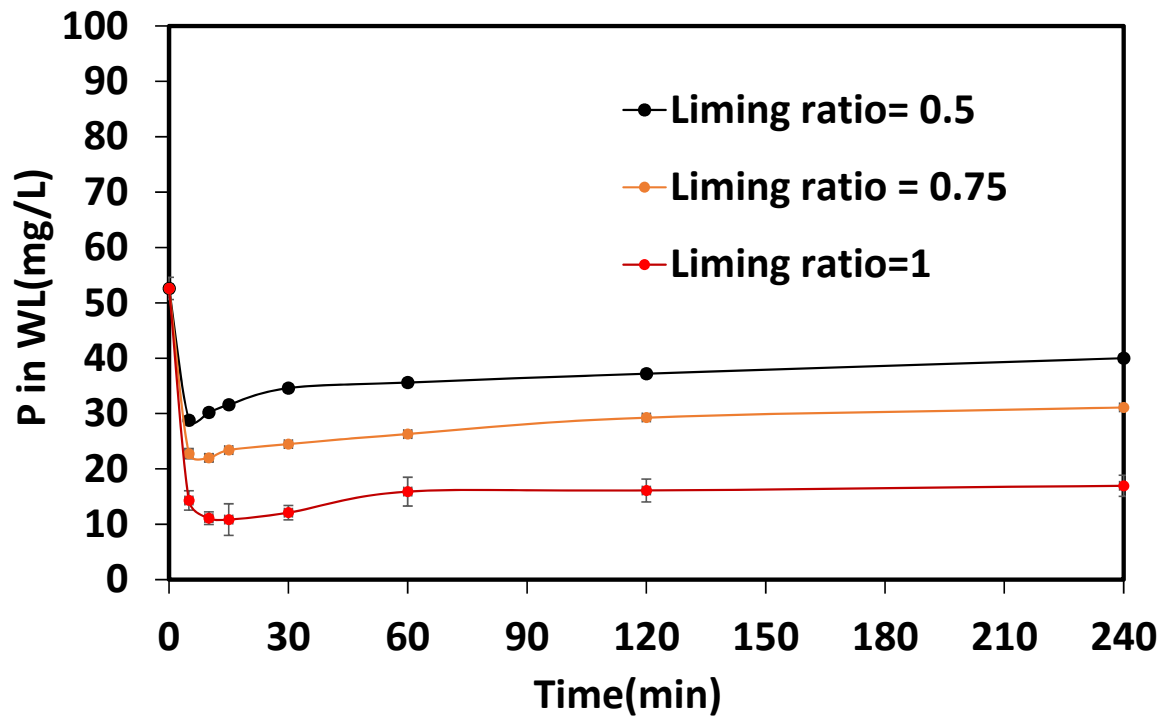
Variable	
TTA	111 g/L Na ₂ O
Sulfidity	14 % (TTA basis)
P concentration	50 mg/L as Na ₃ PO ₄
Liming ratio	0.5 , 0.75 , 1 and 1.5
Slaking and causticizing time	4 h
Lime type	Technical-grade CaO and reburnt lime



Effect of Liming Ratio : Reburnt Lime



Effect of Liming Ratio : Technical-Grade CaO



Conclusions

- P in the reburnt lime can be partially soluble in water during slaking
- For reburned lime, ionic strength can impact uptake of P by lime above an ionic strength of 5.6 M
- The carbonate concentration does not have a clear impact beyond impacting ionic strength.
- P pick-up seems to mostly occur during causticizing
-> Ca(OH)_2 seems to be the active solid
- Reaction for dissolution of rhenanite has been proposed
- P pick-up from the green liquor increases by increasing the liming ratio



Thank You

