Removal of silicon from green liquor with low-temperature precausticizing

XINXING XIA, FANG WANG, SHAN SUN, AND QIAN HU

ABSTRACT: Nonwood materials contain a high percentage of silicon, which causes numerous problems in the chemical recovery section. Researchers previously proposed the method of silicon removal by two-stage causticizing at temperatures of 90°C to 95°C, finding that the desilication rate was about 72.9% and the causticizing efficiency was 22.7% when 30% of the causticizing quicklime (calcium oxide; CaO) was added. The present paper deals with the desilication of green liquor recovered from wheat straw black liquor by a low-temperature precausticization method. The results showed that about 89.3% silicon removal and 10.3% causticizing efficiency were achieved under the following precausticizing conditions: added lime amount of 20%, temperature of 20°C, and reaction time of 60 min. While precausticizing at 90°C with the same lime amount, only about 63.5% silicon removal and 13.0% causticizing efficiency were gained. Therefore, precausticizing with low temperature was beneficial for silicon removal and retention of carbonate (CO_3^{2-}).

Application: Removal of silicon from green liquor with precausticizing at low temperature can effectively increase the desilication rate, which could mitigate the issues caused by "silicon influence" and improve the recycling of lime mud.

Unlike wood, nonwood materials such as wheat straw, reed, and bamboo contain a high percentage of silicon, which causes serious problems in the chemical recovery process [1,2]. Therefore, many researchers have investigated desilication methods. Silicates can be removed from the system by introducing carbon dioxide into the black liquor, converting soluble sodium silicate (Na_2SiO_3) into silica particles that can be separated from the black liquor by sedimentation [3,4]. Approximately 90% of the constituent silicates can be removed from black liquor. However, this separation process is slow because of the small particle size of silica. Runge et al. [5] described the method of removing silicon by a combination of dermal mechanical treatment and caustic chip extraction. However, only about 80% of the silicon was removed. Bohmer [6] proposed the addition of sodium aluminate or bauxite to precipitate the silica as zeolite. High silica removal efficiency was claimed, but the process does not seem to have been developed. Silicon can also be removed by adding carbon dioxide (CO_2) into the green liquor to convert Na_2SiO_3 into calcium silicate [7]. The lime mud can be used as filler after removing silicon. But sodium hydroxide (NaOH) should be added to the green liquor to return to its original pH. Rao et al. [8] proposed two-stage causiticizing whereby silica was selectively precipitated in the first stage and the mud discarded so that relatively clean mud was generated in the second stage. When adding 30% of the causticizing calcium oxide (CaO), commonly referred to as quicklime, to react with green liquor for 30 min at 90°C to 95°C in the first step, only 72.9% of the silicon was removed and the causticizing efficiency was 22.7%. The present paper deals with the desilication of green liquor by a low-temperature precausticization method, since the reaction rate between sodium carbonate (Na_2CO_3) and calcium hydroxide ($Ca(OH)_2$) decreases with temperature [9], which is beneficial for silicon removal.

EXPERIMENTAL

Materials

For these experiments, the green liquor from wheat straw soda pulping was collected from Xingbao Paper Industry Co. Ltd. in Xianyang, Shaanxi Province, China. Calcium oxide was provided by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

Silicon removal process with precausticizing

A certain amount of quicklime and distilled water were added to a flask to slake for 30 min at 80°C. Then, the green liquor was reacted with calcium hydroxide to precipitate silicon. The effect of reaction time, quicklime content, and precausticizing temperature on desilication rate and causticizing efficiency were investigated.

Determination of mixed alkali in green liquor

The concentrations of NaOH and Na_2CO_3 in the green liquor were measured by HCl titration [10].

Determination of silicon content

The silicon content in green liquor was measured with spectrophotometry [11]. The silicon reacts with molybdic acid

Composition	Total Alkali (as NaOH)	Active Alkali (as NaOH)	Sodium Carbonate	Silicon Dioxide
Content, g/L	104.3	11.1	123.5	4.2

I. Analysis of green liquor.

(H_2MoO_4) to form $H_8[Si(Mo_2O_7)_6]$ in weak acidic solutions, and then the silicon-molybdate ligand is converted to $H_8[SiMo_2O_5(Mo_2O_7)_5]$ after reacting with ferrous sulfate ($FeSO_4$). The absorbance of $H_8[SiMo_2O_5(Mo_2O_7)_5]$ was determined with the spectrophotometer at 680 nm. The silicon content was obtained by standard colorimetric analysis.

RESULTS AND DISCUSSION

Analysis of green liquor

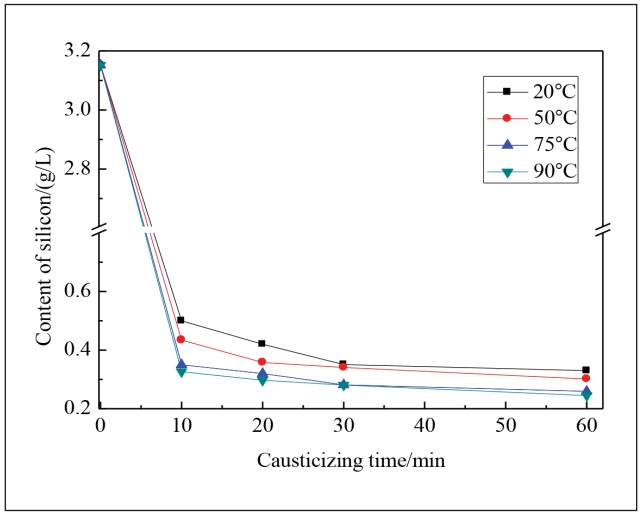
The composition of the green liquor is shown in **Table I**. Sodium carbonate and active alkali were the main ingredients of green liquor. The content of silicon dioxide was 4.2 g/L, which will cause serious problems for the chemical recovery process and the recycling of lime mud.

Effect of temperature on causticizing performance

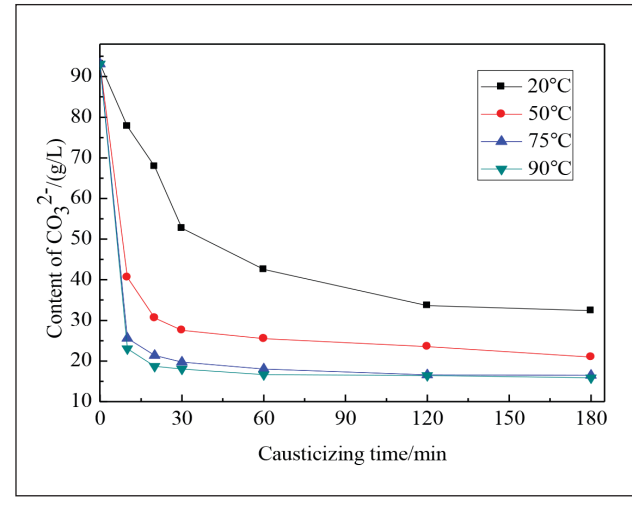
Figure 1 shows the effect of causticizing temperature on silicon content in green liquor with the molar ratio of $Ca(OH)_2$ to Na_2CO_3 of 1:1. No matter how high the reaction temperature, the silicon content in green liquor decreased quickly within the first 10 min, which indicated a fast reaction rate between Na_2SiO_3 and $Ca(OH)_2$. At the same causticizing time, the silicon contents were almost the same when the temperature changed from 20°C to 90°C, which demonstrated that the causticizing temperature had little effect on the reaction rate between Na_2SiO_3 and $Ca(OH)_2$.

Figure 2 shows the effect of causticizing temperature on the content of CO_3^{2-} in green liquor with the molar ratio of $Ca(OH)_2$ to Na_2CO_3 of 1:1. The content of CO_3^{2-} decreased quickly when the reaction temperature increased from 20°C to 90°C at the same reaction time, which indicated that the reaction rate between Na_2CO_3 and $Ca(OH)_2$ was influenced by temperature. When the causticizing time was 10 min, 30 min, and 60 min with the reaction temperature of 20°C, the content of CO_3^{2-} was 77.8 g/L, 52.7 g/L, and 42.5 g/L, respectively. When the reaction temperature raised to 90°C with the causticizing time of 10 min, 30 min, and 60 min, the content of CO_3^{2-} was 23.0 g/L, 18.0 g/L, and 16.7 g/L. Therefore, low-temperature causticization decreased the causticizing reaction rate.

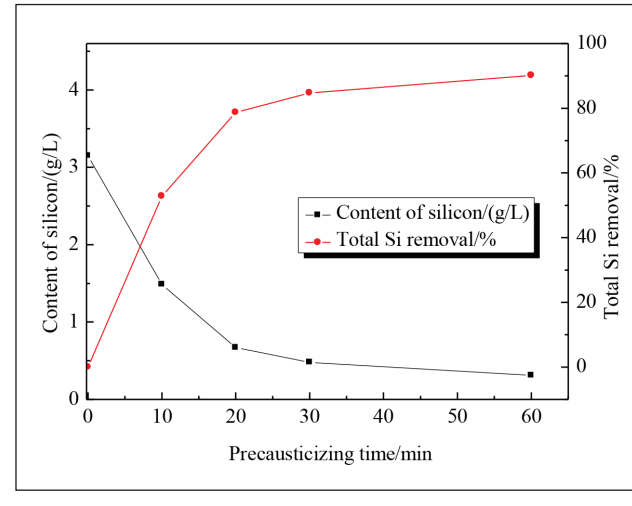
These results demonstrated that the reaction rate between Na_2CO_3 and $Ca(OH)_2$ at high temperature was faster than that



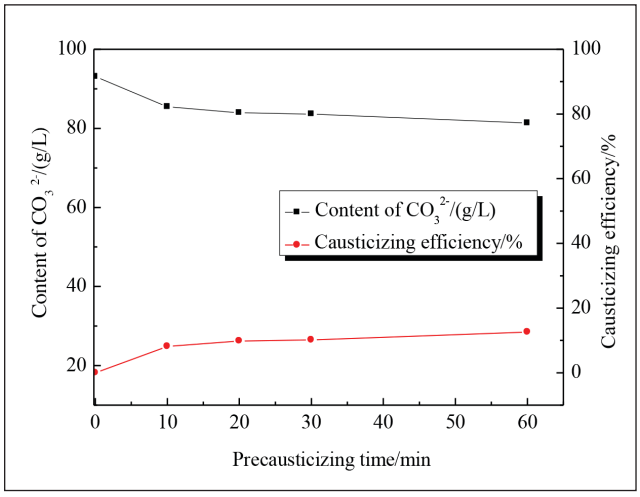
1. Effect of causticizing temperature on silicon content in green liquor.



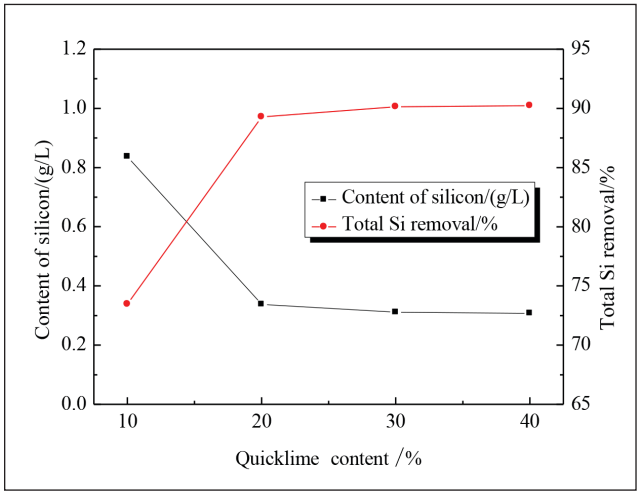
2. Effect of causticizing temperature on the content of carbonate (CO_3^{2-}) in green liquor.



3. Effect of precausticizing time on silicon removal.



4. Effect of precausticizing time on causticizing reaction.



5. Effect of quicklime content on silicon removal.

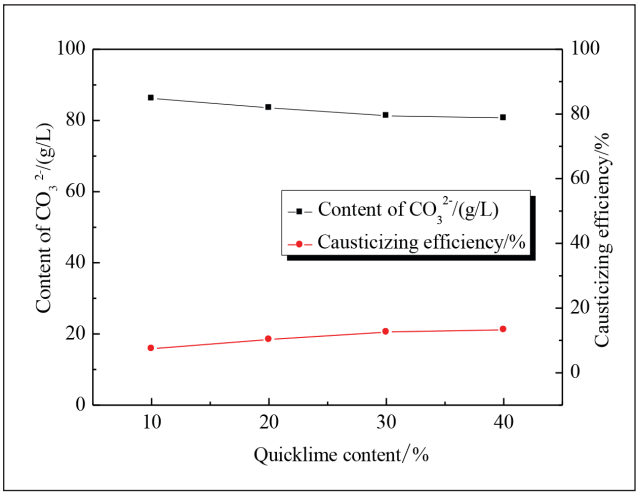
at low temperature. However, reaction temperature had no significant effect on the reaction rate between Na_2SiO_3 and $Ca(OH)_2$. Thus, precausticizing at low temperature could simultaneously remove silicon and retain CO_3^{2-}.

Silicon removal with low-temperature precausticizing

Effect of precausticizing time on silicon removal and causticizing reaction

The silicon was removed by adding 30% of causticizing quicklime to green liquor to selectively precipitate silicon at 20°C. **Figure 3** shows that by increasing precausticizing time, the silicon content in green liquor decreased quickly. The content of silicon reduced to 0.7 g/L, and about 79.0% of silicon was removed when the precausticizing time reached 20 min. The desilication rate slowly increased after about 30 min. About 90.1% of silicon was removed when the reaction time reached 60 min.

Figure 4 shows that the content of CO_3^{2-} in green liquor decreased with increased precausticizing time. The causticizing efficiency increased by 10.2% within the first 30 min. When the reaction time increased from 30 min to 60 min, the causticizing efficiency increased from 10.2% to 12.6%. Causticizing efficiency increased slowly with reaction time. This is because the reaction rate of causticizing decreased at 20°C, which was beneficial to saving CO_3^{2-}. Considering the desilication rate and causticizing efficiency, silicon removal was studied with the reaction time for 60 min.



6. Effect of quicklime content on causticizing reaction.

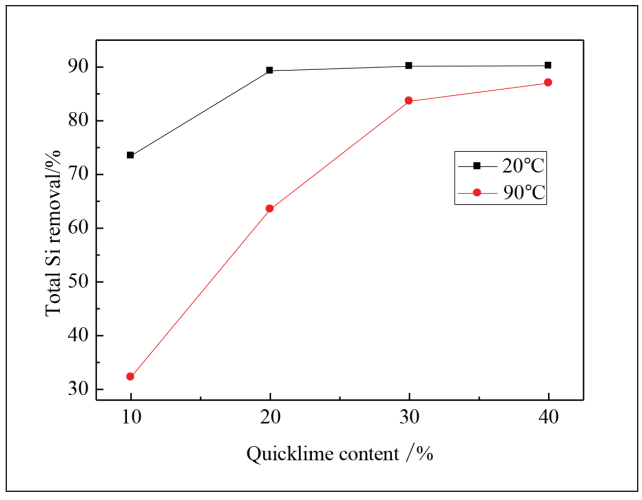
Effect of quicklime content on silicon removal and causticizing reaction

A part of the total quicklime (10% to 40% of stoichiometric ratio) was added to green liquor for precausticizing for 60 min at 20°C. **Figure 5** shows that the desilication rate increased from 73.5% to 89.3% when the content of quicklime increased from 10% to 20%. The removal of silicon increased slowly as quicklime was continuously added. The content of silicon reduced to 0.3 g/L and about 90.2% of the silicon was removed when the quicklime was 40% of the stoichiometric ratio.

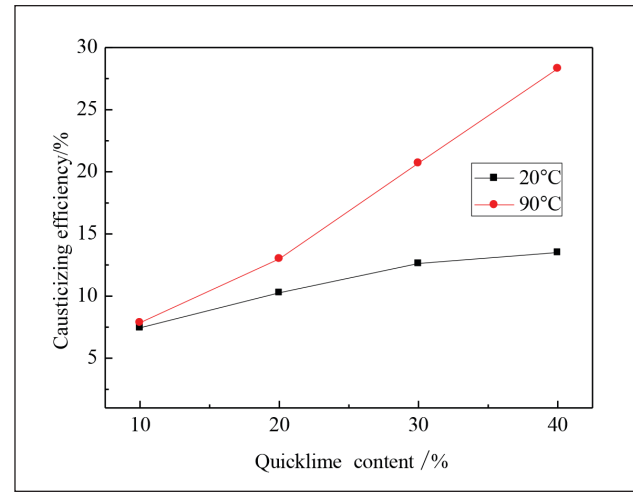
Figure 6 shows that the content of CO_3^{2-} decreased as the quicklime content increased. The causticizing efficiency increased from 7.4% to 12.7% when the quicklime content was increased from 10% to 30%. The causticizing efficiency slowly increased as the quicklime increased to 40% of the stoichiometric ratio. This is because the low temperature decreased the rate of causticizing reaction.

Effect of precausticizing temperature on desilication rate and causticizing efficiency

Figure 7 and **Figure 8** show the effect of precausticizing temperature on desilication rate and causticizing efficiency. As shown in Fig. 7, compared with 20°C, the desilication rate with precausticizing at 90°C was lower under the same reaction conditions. With the increasing of quicklime, this trend was relatively decreased. This is because the reaction rate between $Ca(OH)_2$ and Na_2CO_3 decreased under low temperature conditions, which was beneficial to the reaction be-



7. Effect of precausticizing temperature on desilication rate.



8. Effect of precausticizing temperature on causticizing efficiency.

tween Na_2SiO_3 and $Ca(OH)_2$. Figure 8 shows that the causticizing efficiency increased with increased quicklime content at 20°C and 90°C. The increasing trend of causticizing efficiency at 90°C was obviously higher than that at 20°C. When the quicklime content increased from 20% to 40%, the causticizing efficiency increased by 2.5% and 15.3% at 20°C and 90°C, respectively.

Overall, when 20% of causticizing quicklime was added to removal and 10.3% of causticizing efficiency were achieved. While precausticizing at 90°C with the same added lime amount, only about 63.5% of silicon removal and 13.0% of causticizing efficiency were gained. Therefore, precausticizing at low temperature was beneficial for silicon removal and retention of CO_3^{2-}.

Mills could use the method described here to mitigate the problems of "silicon influence" in the chemical recovery process and improve the recycling of lime mud. Our next step is to identify an industry partner to work with on removing silicon using low temperature precausticizing.

ABOUT THE AUTHORS

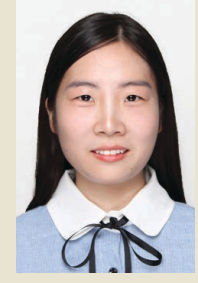
We choose this topic to research because many mills with straw pulping face problems caused by high silicon content of green liquor in the chemical recovery system. While there are many methods of silicon removal, they hardly offer an effective way to achieve high desilication rate.

Previous research studied the method of silicon removal with precausticizing at high temperature, where low desilication rate and high causticizing efficiency were achieved. In this study, silicon was removed with low-temperature precausticizing. Compared with high-temperature precausticizing, the desilication rate increased and causticizing efficiency decreased under the low temperature.

The most difficult aspect of this research was to find out how the causticizing temperature affected the reaction between $Ca(OH)_2$ and Na_2CO_3 and $Ca(OH)_2$ and Na_2SiO_3. We dealt with this by studying the concentrations of SiO_3^{2-} and CO_3^{2-} in green liquor at different causticizing temperatures. We discovered that the causticizing temperature had no significant effect on the reaction rate between Na_2SiO_3 and $Ca(OH)_2$, but it obviously affected the reaction rate between Na_2CO_3 and $Ca(OH)_2$.

Interestingly, we found that when adding 20% of causticizing quicklime to remove silicon with precausticizing for 60 min at 20°C, 89.3% of silicon

Xia



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remove silicon with precausticizing for 60 min at 20°C, 89.3% of the silicon was removed and the causticizing efficiency was only 10.3%. The desilication rate and causticizing efficiency were 63.5% and 13.0% with the same conditions at 90°C. Thus, precausticizing under low temperature achieved high desilication rate and low causticizing efficiency.

CONCLUSIONS

The causticizing temperature had no significant effect on the reaction rate between Na_2SiO_3 and $Ca(OH)_2$, but it obviously affected the reaction rate between Na_2CO_3 and $Ca(OH)_2$. When adding 20% of causticizing quicklime to remove silicon with precausticizing for 60 min at 20°C, 89.3% silicon removal and 10.3% causticizing efficiency were achieved. While precausticizing at 90°C with the same lime amount, only about 63.5% silicon removal and 13.0% causticizing efficiency were gained. Therefore, precausticizing with low temperature was beneficial for silicon removal and retention of CO_3^{2-}. **TJ**

ACKNOWLEDGEMENTS

This work was supported by State Key Laboratory of Pulp and Paper Engineering, South China University of Technology (201509) and Science Foundation of Zhejiang Sci-Tech University (14012081-Y). The authors would like to acknowledge all the assistants in the project group and concerned industrial partners for providing the materials.

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