Low-temperature precausticizing — a hopeful approach for green liquor desilication

XINXING XIA, FANG WANG, XIAOJING QIN, TINGTING TANG, AND TIANWEN ZHOU

ABSTRACT: We investigated silica removal by low-temperature precausticizing and the properties of second causticizing calcium carbonate (CCC). The results showed that about 89.3% of silica removal was achieved when 20% (the stoichiometric ratio) of causticizing quicklime was added for precausticizing at 20°C for 60 min. After that, silica removal became slow. When no precausticizing quicklime was used to remove silica, the CCC particles had a rhombohedral crystal structure covered with amorphous material. As precausticizing quicklime was increased to 30%, the amorphous material and the crack disappeared, and the specific surface area decreased significantly. When CCC was used as filler, the Cobb value decreased significantly, and the sizing effect improved as precausticizing quicklime increased.

Application: Understanding the properties of CCC with different quicklime contents for low-temperature precausticizing, and its effect on paper quality, can mitigate the issues caused by "silica influence" and enable papermakers to reuse CCC produced from the chemical recovery process of wheat straw soda pulping.

Nonwood raw materials, such as wheat straw, bamboo, and reed, contain a moderate amount of silica, which causes serious problems in the chemical recovery process [1,2]. As we described before [3], many researchers [4-8] have tried to find effective ways to remove silica in the pulping process. The most successful approach to silica removal so far seems to be by precipitation from green liquor by partial acidification with carbon dioxide, or by addition of quicklime.

Myreen [9,10] suggested precipitating the silica by introducing carbon dioxide into the black liquor to convert sodium silicate into silica. In this process, about 90% of silica was removed, but foaming, precipitation, and adequate control of pH remained issues. Xia et al. [11] suggested precipitating silica by introducing carbon dioxide into green liquor. About 99% of silica removal was achieved with this method, and precipitation and foaming were no longer a problem, but adequate control of pH remained an issue.

Rao et al. [12] proposed two-stage causticizing to remove silica from green liquor in bamboo pulping. The silica was selectively precipitated in the first step by adding 30% of the causticizing quicklime at about 90°C to 95°C, and the lime mud generated was discarded. In the second step, the rest of the causticizing lime was added and the lime mud generated was calcined for reuse in the causticizing section. About 56% of the silica was removed by the first stage. However, about 44% of silica was left in the lime mud generated in the second stage. The selectivity of the process was not particularly good, and it does not seem to have been developed further. A rather different approach is to precipitate the silica onto the pulp [13]. This gives effective fixing of the silica, but reduces pulp strength, and silica also fixes onto equipment. Consequently, there has been no effective process to remove the silica from the green liquor yet. We investigated low-temperature precausticizing for silica removal, with good results.

EXPERIMENTAL

Materials

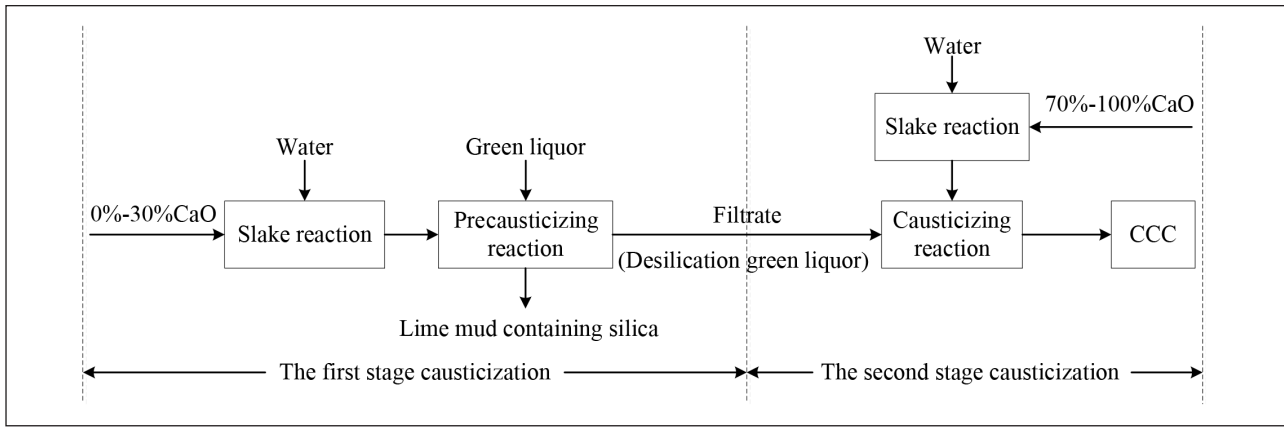
Green liquor from wheat straw soda pulping was collected from Xingbao Paper Industry Co. Ltd. in Xianyang, Shanxi Province, China. Calcium oxide was provided by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

Determination of silica content in green liquor

The content of silica in green liquor was measured with spectrophotometry [14]. In weak acidic solutions, silica reacts with complex agent of ammonium molybdate to form silicon-molybdate ligand. The ligand is then reduced by ferrous sulfate to form $H_8[SiMo_2O_5(Mo_2O_7)_5]$. The absorbance of $H_8[SiMo_2O_5(Mo_2O_7)_5]$ was measured at 680 nm using a 722S spectrophotometer (Shanghai Arris Light Technology Co. Ltd.; Shanghai, China). The silica content was obtained by colorimetric analysis.

Two-stage causticization

Figure 1 shows a diagram of two-stage causticization. In the first stage (precausticization), a part of the total quicklime requirement (0% to 30% of the stoichiometric ratio) was



1. Diagram of two-stage causticization.

mixed with distilled water at a quicklime concentration of 20% by weight to prepare milk of lime using a slaking temperature of 80°C and reaction time of 30 min. Then green liquor was reacted with calcium hydroxide to remove silica. The precausticizing was done at 20°C with constant stirring for 60 min. At the end of the reaction time, the causticized slurry was filtered, and the filtrate was used for the second stage causticization. In the second stage, the filtrate obtained from the first stage was causticized with the slaked lime. The second stage used a filtrate loading rate of 0.094 mL/s, loading period of 90 min, temperature of 80°C, and stirring speed of 300 rpm. After the reaction, the CCC was washed with water until neutral, then subjected to quality analysis.

Characterization of the CCC

The crystal forms of the CCC were examined with a D/MAX-1200 X-ray diffraction (XRD) analyzer (Rigaku Corporation; Tokyo, Japan), and the morphology of CCC was visualized with a Quanta 200 scanning electron microscope (FEI; Eindhoven, The Netherlands). The specific surface area was measured with a Micromeritics Instrument Corporation (Norcross, GA, USA) Gemini VII surface area analyzer. Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific; Waltham, MA, USA) using potassium bromide pellets.

Handsheet preparation

To a bleached hardwood kraft pulp, 0.15% of alkyl ketene dimmer as sizing agent, 20% of CCC as filler, 0.05% of cationic polyacrylamide, and 0.2% of bentonite as retention agents were added in sequence under mixing. Then, laboratory paper sheets (handsheets) were formed with a sheet former. Cobb value was determined according to TAPPI Standard Test Method T 441 om-09 "Water absorptiveness of sized (non-bibulous) paper, paperboard, and corrugated fiberboard (Cobb test)."

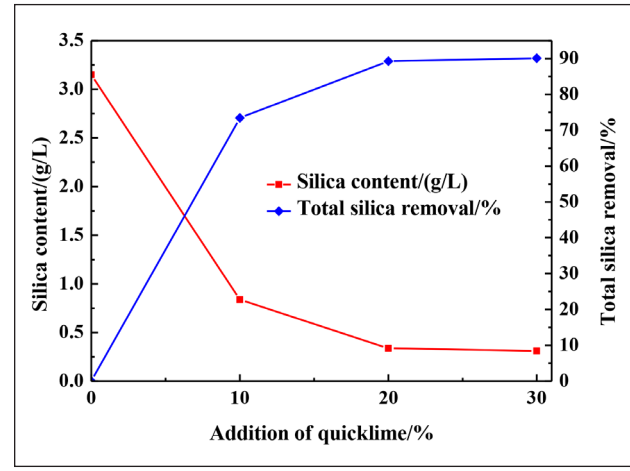
RESULTS AND DISCUSSION

Analysis of green liquor

Table I shows the composition of the green liquor. Sodium carbonate and active alkali were the main components of the green liquor. The content of silica was 4.2 g/L, which will cause serious problems in the recycling of lime mud.

Effect of low-temperature precausticizing on silica removal

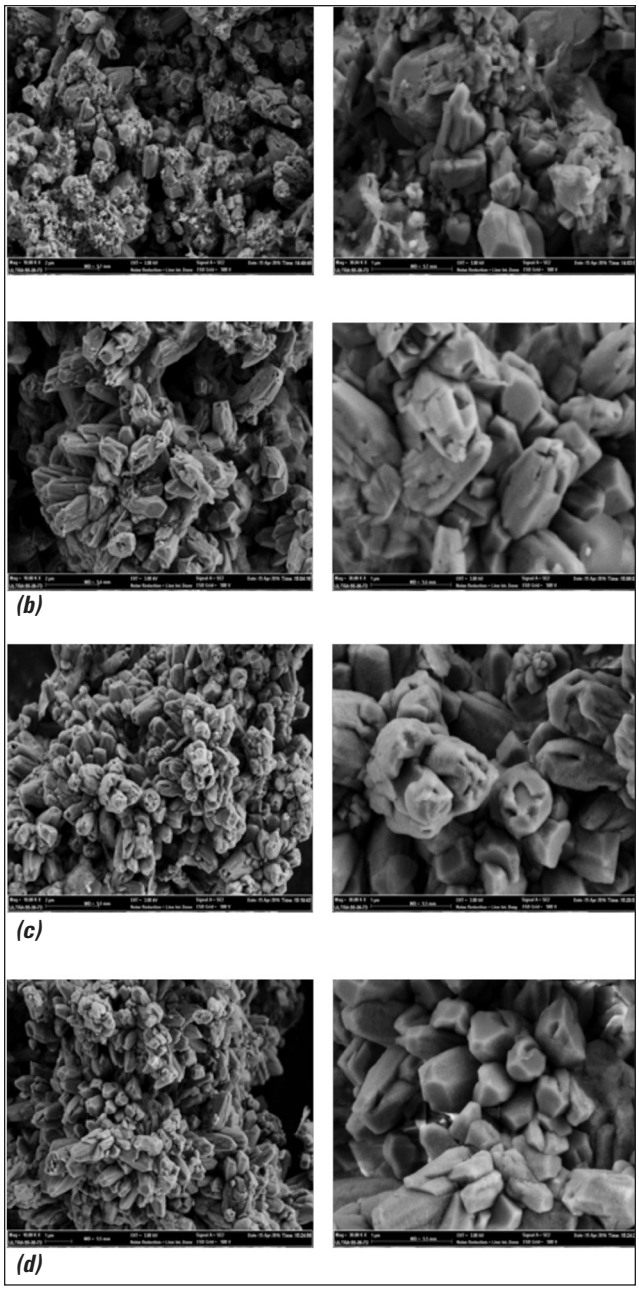
As Rao et al. [12] described, during two-stage causticization, silica is preferentially precipitated, followed by causticization when quicklime is added. This can be attributed to the faster rate of reaction between sodium silicate and calcium hydroxide compared with that between sodium carbonate and cal-



2. Effect of addition of precausticizing quicklime on silica removal.

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

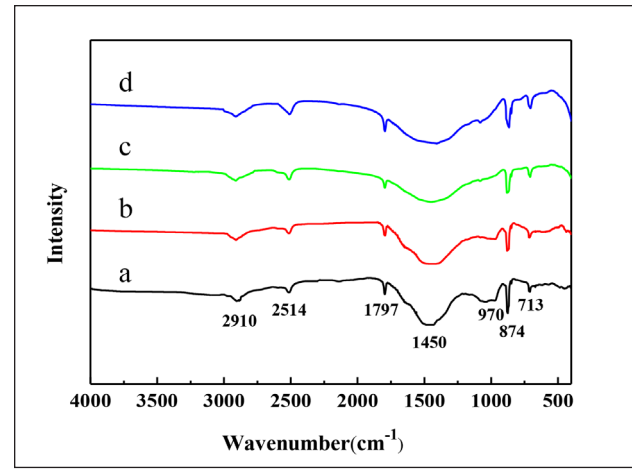
I. Analysis of green liquor.



3. Scanning electron microscope (SEM) images of causticizing calcium carbonate (CCC) with different added amounts of precausticizing quicklime: a = 0% of causticizing quicklime, b = 10% of causticizing quicklime, c = 20% of causticizing quicklime, d = 30% of causticizing quicklime.

cium hydroxide. Low temperature reduces the causticizing reaction rate between sodium carbonate and calcium hydroxide, which is beneficial to the reaction between sodium silicate and calcium hydroxide [15].

A part of the causticizing quicklime (0% to 30% stoichiometric ratio) was added to the green liquor at 20°C for precausticization. **Figure 2** shows that about 73.5% of silica was removed when 10% of quicklime was added. The desilication rate increased to 89.3% when the quicklime



4. Fourier transform infrared (FTIR) spectroscopy spectra of CCC with different added amounts of precausticizing quicklime: a = 0%, b = 10%, c = 20%, d = 30%.

dosage increased to 20%; after that, silica removal became slow. About 90.1% of silica removal was achieved when 30% of quicklime was used.

Morphology of CCC with low-temperature precausticizing

The chemical reactions during causticizing are as follows:

$$Ca(OH)_2+Na_2CO \rightarrow OaOH_3+2NaOH \quad (1)$$

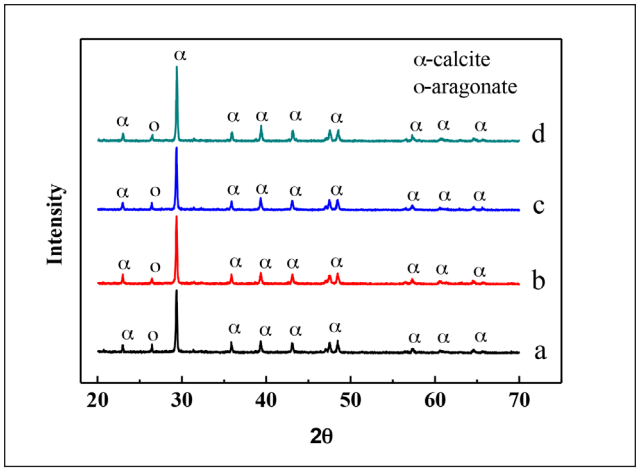
$$Ca(OH)_2+Na_2SiO_3+H_2OHOOH \rightarrow SiO_2 \rightarrow H_2O+2NaOH \quad (2)$$

The first and second reactions take place simultaneously, so the calcium silicate is generated with the calcium carbonate in the causticizing process. The morphology of CCC is not only affected by the causticizing reaction, but also by the calcium silicate generation.

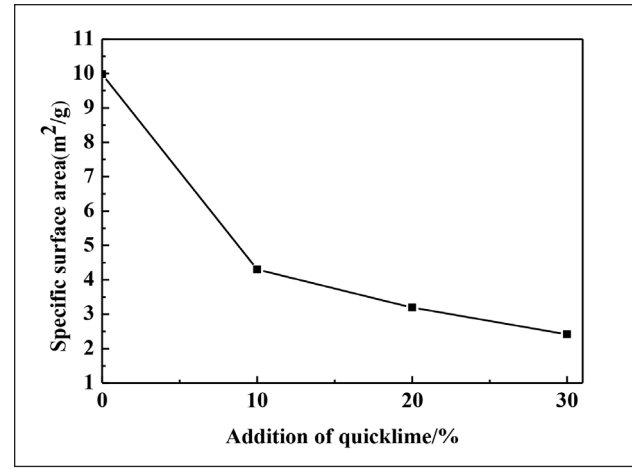
Figure 3 shows the morphology of the CCC formed in the second causticizing process after low-temperature precausticization. When no precausticizing quicklime was used to remove silica, the CCC particles had a rhombohedral crystal structure covered with amorphous material (Fig. 3a). As 10% of precausticizing quicklime was used (Fig. 3b), the amorphous material almost disappeared and the CCC particles had a rhombohedral crystal structure with cracks on the surface. The same was true with 20% of precausticizing quicklime (Fig. 3c). As the precausticizing quicklime was increased further, to 30% (Fig. 3d), the amorphous material disappeared completely, and the CCC particles had a clear rhombohedral crystal structure with no crack.

FTIR spectrum

FTIR is an effective method to evaluate the presence and the extent of silica in CCC. As shown in **Fig. 4**, the bands at 1450 cm^{-1} ($V_3(CO_3)$), 874 cm^{-1} ($V_2(CO_3)$), and 713 cm^{-1} ($V_4(CO_3)$) belong to the characteristic calcium carbonate absorption



5. X-ray diffraction (XRD) analyzer spectra of CCC with different added amounts of precausticizing quicklime: a = 0%, b = 10%, c = 20%, d = 30%.



6. Specific surface area of CCC with different added amounts of precausticizing quicklime.

bands [16]. The band at 970 cm^{-1} is the result of symmetric stretching of the Si–O-Si bonds [17]. When the precausticizing quicklime was 0% and 10% of the stoichiometric ratio, the band at 970 cm^{-1} was clearly observed. As the precausticizing quicklime increased to 30%, the band at 970 cm^{-1} disappeared, proving that the silica was almost totally removed.

Crystal forms of CCC

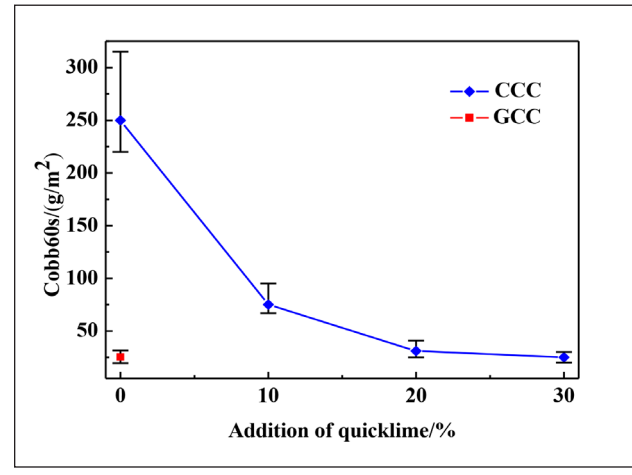
The crystal forms of the CCC were measured by powder XRD. As shown in **Fig. 5**, no matter how much of the precausticizing quicklime was added, the crystals of CCC were both calcite and aragonite [18-19]. The characteristic absorption peak of calcium silicate was not observed. This suggested that the calcium silicate itself did not polymerize to form crystal. However, as shown in Fig. 2 (especially Fig. 2a), some amorphous material was in the CCC. Amorphous basically means non-crystalline. As such, it cannot be detected by XRD analysis. It is likely that the amorphous material was calcium silicate hydrate gel, a well-known compound present in hydrated cement (concrete).

Specific surface area of CCC

The specific surface area of the CCC was tested with the low-temperature nitrogen adsorption method. As the added amount of quicklime for precausticization was increased, the specific surface area of the CCC decreased rapidly (**Fig. 6**). The specific surface area of un-precausticizing CCC was 9.98 m^2/g. As the precausticizing quicklime increased to 30% of the stoichiometric ratio, the specific surface area decreased by nearly 76%, to 2.41 m^2/g. This was the result of the change in morphology of the CCC caused by the removal of silica in the precausticizing process.

Effect on paper sizing of CCC with low-temperature precausticizing

As shown in **Fig. 7**, as precausticizing quicklime increased, the Cobb value decreased rapidly and the sizing effect improved. When the precausticizing quicklime increased from 0% to 20%,



7. Effect of precausticizing quicklime addition on paper sizing degree (CCC = causticizing calcium carbonate; GCC = ground calcium carbonate).

the Cobb value decreased from 250.3 g/m^2 to 31.2 g/m^2, which met the sizing requirement for fine paper. This resulted from the presence of hydroxyl in calcium silicate hydrate, which increased the hydrophilicity of the CCC. In addition, the high surface area and porosity of CCC with high silica content increased the absorption of alkyl ketene dimers, thus leading to the difficulty of sizing [20]. When the added amount of precausticizing quicklime increased to 30%, the Cobb value was 25.1 g/m^2. Therefore, low-temperature precausticizing is an effective method to remove silica from green liquor.

CONCLUSIONS

When 20% (the stoichiometric ratio) of quicklime was added for precausticizing at 20°C for 60 min, about 89.3% of silica removal was achieved; after that, silica removal became slow. When no precausticizing quicklime was used to remove silica, the CCC particles had a rhombohedral crystal structure covered with amorphous material. When the precausticizing quicklime was increased to 30%, the amorphous material and

the crack disappeared, and the specific surface area decreased significantly. When the CCC was used as filler, with the increasing of precausticizing quicklime, the Cobb value decreased significantly and the sizing effect improved. **TJ**

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ABOUT THE AUTHORS

We chose this topic to research because many mills with nonwood materials face problems caused by high silica content in green liquor during chemical recovery. We tried to remove silica with low-temperature precausticizing and had amazing results.

Previous research studied the method of silica removal with precausticizing at high temperature, which had lower desilication rate than that at low temperature.

The most difficult aspect of this research was to find out how precausticizing quicklime affects the properties of causticizing calcium carbonate (CCC) and paper quality when used as filler. We accomplished this with characterization methods that included scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, surface area, and Cobb value of paper.

We discovered that when 20% quicklime (the stoichiometric ratio) was added for precausticizing for 60 min at 20°C, about 89.3% of silica removal was achieved; after that, silica removal became slow.

We found that CCC particles all formed with calcite and aragonite. As the precausticizing quicklime increased, the amorphous material and the crack disappeared, and the specific surface area decreased significantly. When the CCC was used as filler, with the increasing of precausticizing quicklime, the Cobb value decreased significantly and the sizing effect obviously improved.

Mills could use this method to mitigate the problems of "silica influence" in the chemical recovery process and improve the recycling of lime mud.

Our next step is to find an industry partner to work with on removing silica with low-temperature precausticizing.

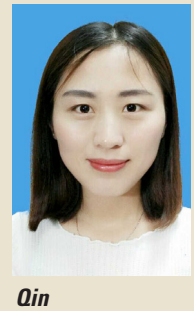
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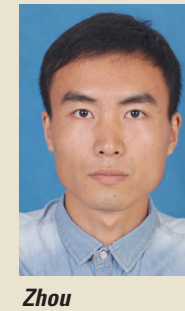
Wang



Qin



Tang



Zhou