Effect of silicon on properties of causticized calcium carbonate produced in wheat straw soda pulping

XINXING XIA, XING WANG, MINGZHU DU, AND ZHAOQING LU

ABSTRACT: Green liquor in the chemical recovery process of wheat straw pulping was treated with carbon dioxide to precipitate silicon. We report on the properties of causticized calcium carbonate (CCC) with different silicon contents, as well as its impact on paper quality when used as filler. The research results showed that silicon content had no significant effect on the crystal form of CCC, and all crystals were formed as calcite. Calcium silicate itself did not polymerize to form crystal in the course of causticization. Instead, silicon existed as a solid solution in CCC. The morphology of CCC changed gradually from amorphous to square with the decrease of silicon content. The brightness of CCC increased slightly and the average particle size tended to grow after removal of silicon. When 97% of silicon was removed and the average particle size reached 6.84 μm, the specific surface area and sedimentation volume decreased gradually as the desilication rate increased. When CCC was used as filler and silicon in CCC decreased, opacity remained nearly the same and brightness increased slightly; however, the Cobb value decreased significantly and the sizing efficiency obviously improved. When the silica content decreased to 3.2% the Cobb value was 27.7 g/m^2, which reached the standard for fine paper sizing. The tear strength increased gradually, while the tensile strength decreased with the reduction of silicon.

Application: Understanding the properties of causticized calcium carbonate with different silicon content, as well as its impact on paper quality, can benefit papermakers seeking to reuse causticized calcium carbonate produced from the chemical recovery process of straw soda pulping.

Due to the shortage of wood resources, nonwood materials such as straw, bamboo, and reed are still widely used in Europe and Asia. However, these nonwood raw materials contain up to 6% silicon. In many pulping processes, including kraft and soda (alkali) processes, silica builds up in the black liquor. In most processes, the black liquor is sent to a recovery boiler; however, the buildup of silica in a recovery boiler lowers its efficiency [1]. In the causticizing process, sodium silicate reacts with calcium hydroxide to form calcium silicate, which makes recycling of lime difficult and reduces the activity of lime when the lime mud is calcined [2]. Currently, no commercial process exists to reuse the causticized calcium carbonate (CCC) with a moderate amount of silica.

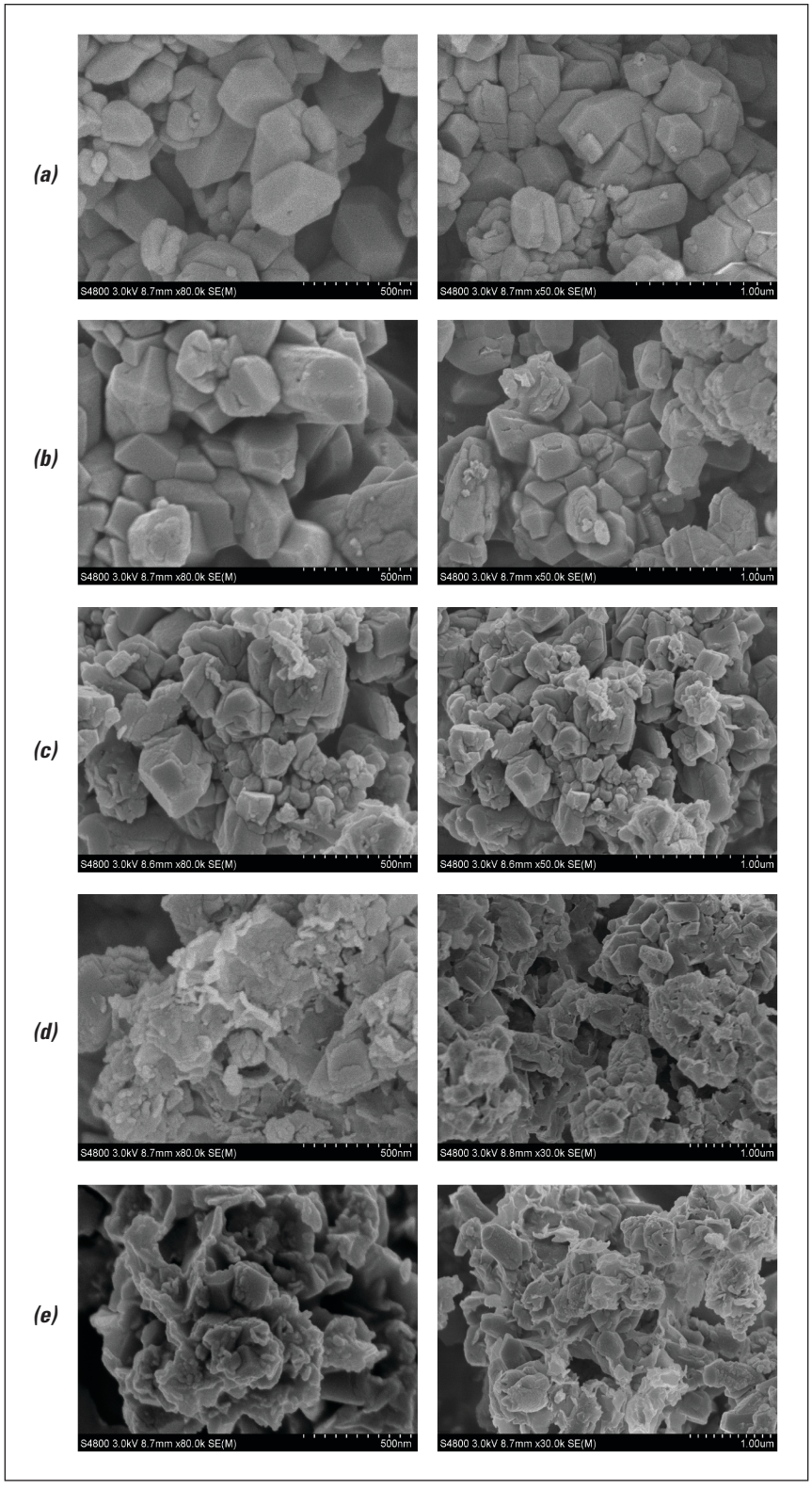
Many researchers have studied the problems caused by silicon. Gupta et al. [3] described a method whereby about 75% of the silica could be extracted from bagasse with 2% sodium hydroxide at 75°C. The method looks very attractive but does not appear to have progressed beyond the laboratory stage. Myreen [4,5] studied the process of silicon removal by introducing carbon dioxide (CO_2) into the black liquor to convert sodium silicate into silica, which could be separated from the black liquor. In this process, about 90% of silicon was removed; however, the calcium silicate particles were very small so the particles were suspended in solution and difficult to precipitate. Rao et al. [6] 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. However, the selectivity of the process was not particularly good and it does not seem to have been developed further. Bohmer [7] proposed the addition of sodium aluminate or bauxite to precipitate silica as zeolite. High silica removal efficiency was claimed but the process does not seem to have been developed. A rather different approach is to precipitate the silica onto the pulp [8]. This gives effective fixing of the silica but reduces pulp strength, and silica also fixes onto equipment.

In summary, there is no popular commercially proven method for selective removal of silica. Therefore, we should perhaps change the way of thinking and look for a method of reusing lime mud with moderate silica content rather than studying how to remove silica. Thus far, little research is available on the performance and usage of lime mud containing moderate amounts of silicon.

EXPERIMENTAL

Materials

For these experiments, the green liquor from wheat straw



1. Scanning electron microscope (SEM) photograph of causticized calcium carbonate (CCC) with different silica contents: (a) 0.31% silica content, morphology was regular square; (b) 1.28% silica content, morphology was also regular square; (c) 3.20% silica content, square shape began to disappear; (d) 5.18% silica content, square disappeared and CCC became amorphous schistosity; (e) 6.40% silica content, square disappeared and CCC became amorphous schistosity.

soda pulping was collected from Aohui Paper Industry Co. Ltd. in Xi'an, Shaanxi Province, China. Calcium oxide was provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The composition of green liquor was analyzed with IRIS Intrepid II ICP-AES (Thermo Scientific; Waltham, MA, USA); the results are shown in **Table I** [9].

Silicon removal process from green liquor

Carbon dioxide was introduced into 200 mL of green liquor with the following conditions: CO_2 flow rate of 0.3 L/min, reaction temperature of 80°C, stirring speed of 350 rpm, and CO_2 introducing time of 20 min. Then silica was separated by precipitation, and green liquor with a silica removal rate of 97% was obtained [9]. Green liquors with different silicon contents were obtained by mixing raw green liquor and silicon-removed green liquor in different proportions.

Preparation of CCC

In a 500-mL flask, quicklime and distilled water were mixed to a quicklime concentration of 10% by weight to prepare lime milk under the following conditions: slaking temperature of 80°C and reaction time of 20 min. Then the slaked lime was causticized with green liquors with different silicon contents under the following conditions: green liquor loading rate of 0.094 mL/s, loading period of 90 min, temperature of 80°C, and stirring speed of 350 rpm. After the reaction, the CCC was washed with water till neutral and then subjected to quality analysis.

Determination of particle size and sedimentation volume

The particle size of CCC was analyzed with the BT-9300H type laser particle size analyzer (Bettersize Instruments Ltd.; Dandong, China). To determine sedimentation volume, 100 mL of distilled water containing 10g of CCC was put into a 100-mL measuring cylinder and shaken well. The cylinder was placed upright, and the interface height of the precipitate was recorded after 3 h.

Composition	Total Alkali	Active Alkali	Sodium Carbonate	Silicon Dioxide
Content (g/L)	117.2	34.3	82.7	7.4

I. Analysis of green liquor.

Measure of CCC crystal forms and morphology

Crystal forms of CCC were measured using the D/MAX-1200 X-ray diffraction analyzer (Rigaku Corp.; Tokyo, Japan), and the morphology of CCC was measured with a scanning electron microscope (SEM).

Handsheet preparation

To hardwood bleached kraft pulp with CSF of 425 mL, researchers added and stirred 0.2% of sizing agent (alkyl ketene dimer [AKD]), 20% of CCC as filler, and 0.05% of CPAM/0.2% bentonite as a retention and drainage agent. Then handsheets were formed in a handsheet former.

RESULTS AND DISCUSSION

Morphology of CCC with different silicon contents

The green liquor of wheat straw pulping contains carbonate (CO_3^{2-}) and silicate (SiO_3^{2-}). In the causticizing process, three reactions take place, as shown in Eqs. (1, 2) [10], and Eq. (3) [11]:

$$CaO+H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2+Na_2CO_3 \rightarrow CaCO_3+2NaOH \quad (2)$$

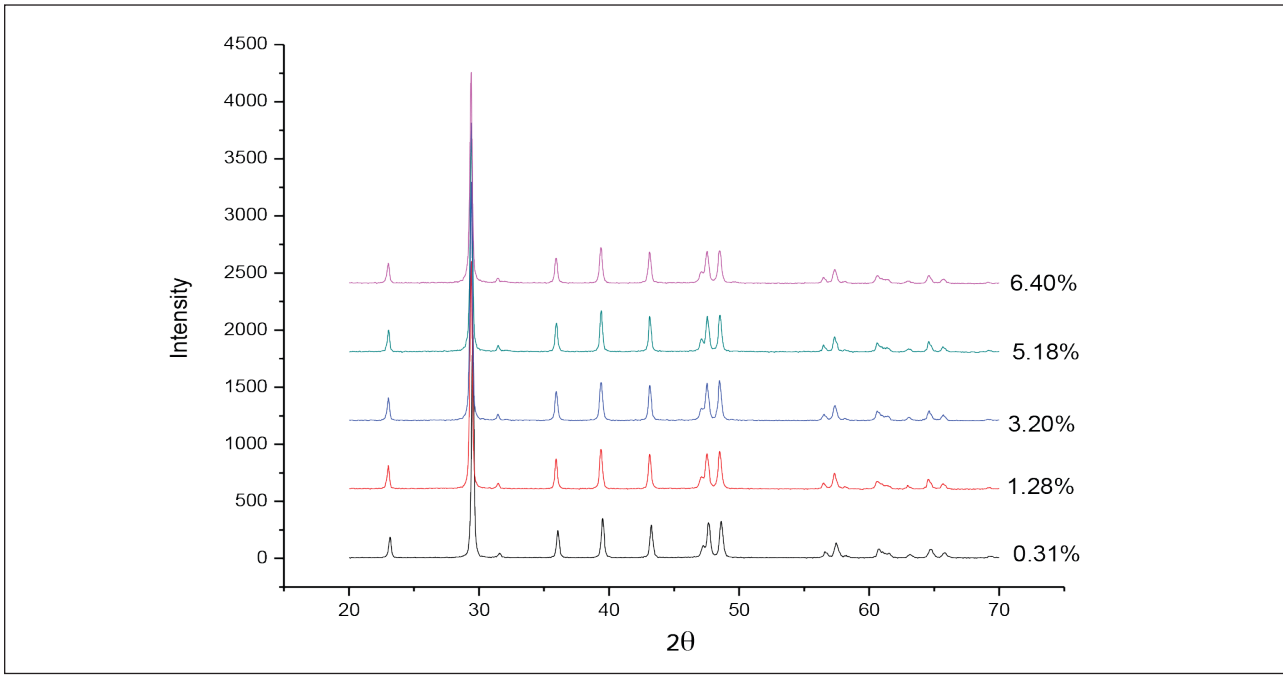
$$Ca(OH)_2+ Na_2SiO_3+H_2O \rightarrow CaO\cdot SiO_2\cdot H_2O+2NaOH \quad (3)$$

The second and third reactions take place at the same time, so the calcium silicate hydrate is also generated along with the calcium carbonate in the causticization process. Therefore, the morphology of CCC is affected by the causticizing reaction conditions as well as by the generation of the calcium silicate hydrate.

The morphology of CCC formed in the causticizing process with different silicon contents is shown in **Fig. 1**. When the silica contents were 0.31% (Fig. 1a) and 1.28% (Fig. 1b), the shapes of CCC were square. While the silica content increased to 3.20% (Fig. 1c), the morphology of CCC became irregular because of the inducement of silicon, but the square shape could still be seen. When the silica content was 5.18% (Fig. 1d) and 6.40% (Fig. 1e), the square shape disappeared and CCC turned into amorphous schistosity.

Effect of silicon content on crystal forms of CCC

The polymorphic forms of CCC produced were investigated by the powder X-ray diffraction (XRD) method. As shown in **Fig. 2**, peaks at 2θ of 23°, 30°, 36°, 40°, 43°, 47°, and 48°, respectively, correspond to the calcium carbonate crystal planes of (012), (104), (110), (113), (202), (018), and (116), which all belong to the calcite crystal characteristic absorption peaks [12]. According to the XRD spectra, it can be seen that no matter what the silica content, the CCC was calcite crystal and the calcium silicate itself didn't polymerize to form crystal. Therefore, silicon existed in the form of solid solution in CCC.



2. X-ray diffraction (XRD) spectra of causticized calcium carbonate with different silica contents.

SiO_2 content in CCC, %	6.40	5.18	3.20	1.28	0.31
Brightness, %	90.3	90.7	90.9	91.3	91.7
Average particle size, μm	5.13	4.96	4.51	5.50	6.84
Surface area, $m^2 \cdot kg^{-1}$	677.72	528.10	511.40	502.12	435.37
Sedimentation volume, mL·g-1	2.80	2.60	2.55	2.29	2.26

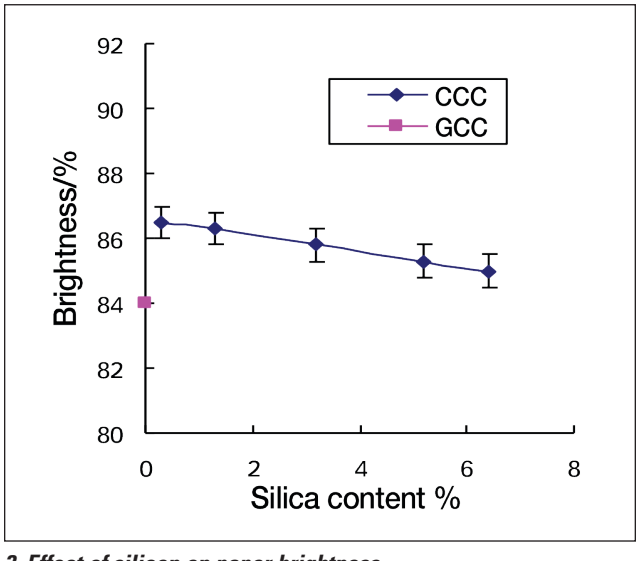
II. Effect of silicon contents on CCC physical properties.

Effect of silicon content on CCC physical properties

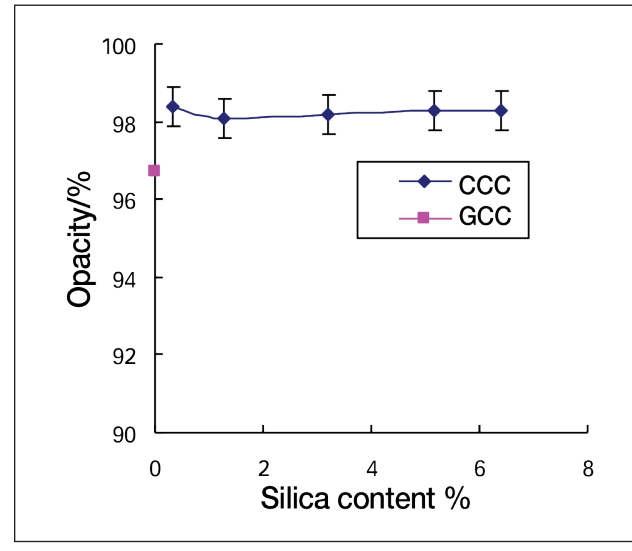
Table II shows the physical properties of CCC produced with green liquors with different silicon content. As silicon content decreased, the brightness of CCC increased slightly. When the silica content was 6.4%, the brightness was 90.3%; when the silica content was reduced to 0.31%, the brightness increased to 91.7%. The average particle size of CCC increased with the reduction of silica. When the silica content was 0.31%, the average particle size reached 6.84 μm. The specific surface area and sedimentation volume decreased with the reduction of silica, which was due to the change of morphology and particle size of CCC. As shown in SEM photograph (Fig. 2), the morphology of CCC became more regular and the average particle size increased as silica was reduced.

Effect of CCC with different silicon content on paper quality

The effects of CCC with different silicon content on paper brightness when used as filler are shown in **Fig. 3**. The brightness increased with the reduction of silica, and was higher in all instances than when commercial ground calcium carbonate (GCC) was used. When the silicon content was reduced from 6.40% to 0.31%, brightness increased by 1.5%. Therefore, after the carbon dioxide acidification process to precipitate silicon, some metal ions in green liquor, such as Fe^{3+}, Mg^{2+}, generated into silicate and were removed. The silicon almost had no impact on the opacity of the paper, as shown in **Fig. 4**, but opacity was higher than when commercial GCC was used.



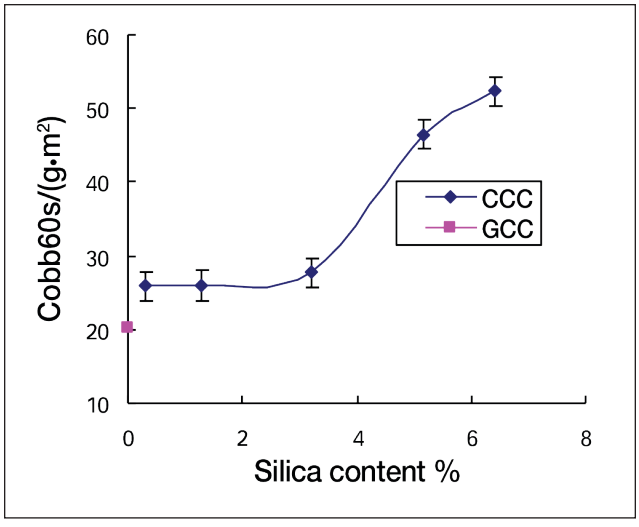
3. Effect of silicon on paper brightness.



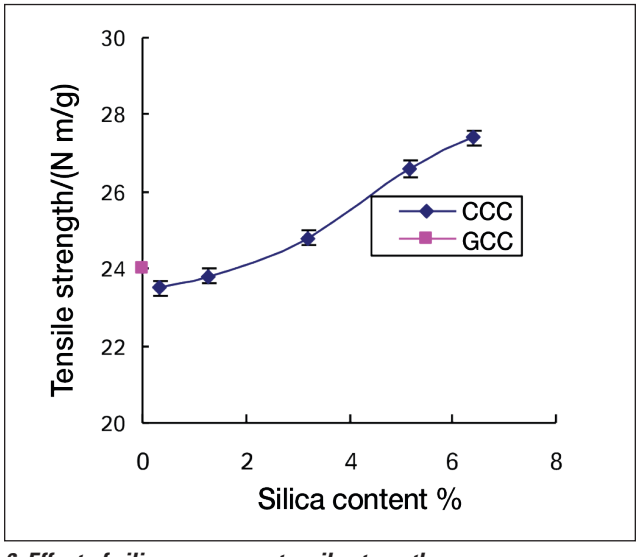
4. Effect of silicon on paper opacity.

As shown in **Fig. 5**, with the decrease of silicon content in CCC, the Cobb value decreased rapidly and the sizing effect obviously improved. In particular, when the silica content was reduced from 5.18% to 3.2%, the Cobb value decreased from 46.5 g/m² to 27.7 g/m², meeting the sizing requirement for fine paper. This was due to the presence of hydroxyl in calcium silicate hydrate, which increased the hydrophilicity of CCC. In addition, the high surface area and porosity of high-silicon CCC increased the absorption of AKD, thus leading to the difficulty of sizing [13]. When the silica content decreased to 0.31%, the Cobb value was 25.9 g/m²; therefore, silicon had a significant performance on sizing efficiency.

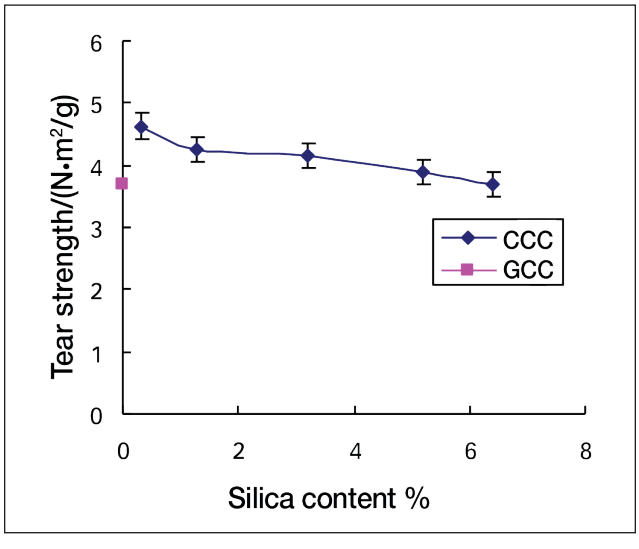
The main factors affecting the tensile strength of paper are the bonding force among the fibers, fiber strength, fiber length, and interlacing, with the bonding force being the decisive factor. As shown in **Fig. 6**, with the decrease of silicon



5. Effect of silicon on paper sizing degree.



6. Effect of silicon on paper tensile strength.



7. Effect of silicon on paper tear strength.

content, the tensile index of the paper reduced gradually. The tensile index was 27.4 N.m/g when the silicon content was 6.4% and decreased to 23.5 N.m/g when the silicon content was 0.31%. It is probably due to the hydrogen bonds between the hydroxyl of calcium silicate hydrate and fibers, which increased the tensile strength..

The main factors affecting the tear strength of paper are fiber morphology, including fiber length, thickness, and stiffness, followed by hydrogen bonding numbers between fibers. Furthermore, increasing the paper porosity can improve the tear strength [14]. As shown in **Fig. 7**, with the decrease of silica content, paper tearing index increased. The tear index was 3.69 N.m²/g when the silicon content was 6.4% and 4.63 N.m²/g when the silica content of CCC was 0.31%. The explanation is that the regular shaped CCC increased the paper porosity more than the amorphous CCC.

CONCLUSIONS

Silicon content had no significant effect on the crystal form of CCC; all crystals formed as calcite. Calcium silicate itself did not polymerize and crystallize. Silicon existed in the form of solid solution in CCC. The morphology of CCC changed gradually from amorphous to square with the reduction of silicon content.

With the reduction of silicon content in CCC, brightness and average particle size increased slightly. The average particle size reached 6.84 μm when 97% of silicon was removed. As the desilication rate increased, the specific surface area and sedimentation volume decreased gradually.

When the CCC was used as filler and the silicon content in CCC decreased, the opacity of the paper remained nearly the same, brightness increased slightly, the Cobb value decreased significantly, and the sizing effect improved. When the silica content decreased to 3.20%, the Cobb value was 27.7 g/m², which reached the threshold for fine paper sizing. The tear strength increased gradually as the desilication rate increased, and the tensile strength decreased. **TJ**

ACKNOWLEDGEMENTS

This work was part of a research project sponsored by State Key Laboratory of Pulp and Paper Engineering, South China University of Technology (201241). The authors acknowledge all the assistants in the project group and industrial partners who provided the materials.

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ABOUT THE AUTHORS

We chose to do this research because many mills with straw pulping face the problems caused by high silicon content of green liquor in the chemical recovery process. Currently, there is no popular commercially proven method for the reuse of causticized calcium carbonate (CCC) with a moderate silicon content.

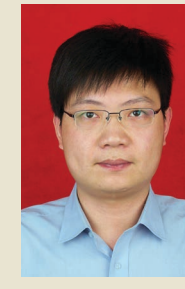
Previous research was based mainly on the one-step process and the seeding process to remove silicon from green liquor. In our work, we mainly investigated the possibilities of using CCC with different silicon content as papermaking filler.

The most difficult aspect of this research was to find out how the silicon existed in the CCC and how the silicon affected the CCC. We addressed that with the X-ray diffraction analyzer and SEM. We found that the silica content had no significant effect on the crystal form of CCC, and crystals were formed as calcite in all cases. The morphology of the CCC changed gradually from amorphous to square as the silica content decreased. When the CCC was added to paper as filler and the silica in the CCC decreased, the Cobb value decreased significantly and the sizing efficiency obviously improved.

Xia

Wang

Du



Lu

Understanding the properties of CCC with different silicon contents, as well as its impact on paper quality, can help papermakers to try to reuse CCC. Our next step is to find a mill to work with on reusing CCC.

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