

Removal of silicon from green liquor with carbon dioxide in the chemical recovery process of wheat straw soda pulping

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ABSTRACT: Green liquor in the chemical recovery process of wheat straw pulping was treated with carbon dioxide to precipitate silicon by a one-step process and a seeding process to address problems caused by high silicon content. The total silicon removal, the particle size, and the sedimentation performance of silica were investigated. The results showed that the pH of green liquor decreased with increasing amounts of carbon dioxide, becoming stable after the pH decreased to 8.2. Reaction temperature had no significant effect on the removal of silicon. About 99% of silicon removal was achieved at a pH of 9.2 at room temperature. In the one-step process, the particle size increased and the silica sedimentation performance improved with decreasing pH. The particle size decreased and the sedimentation performance improved with increasing reaction temperature. At a pH of 9.5 and reaction temperature of 80°C, the particle size was 10.43 μm . In the seeding process, 40% green liquor was treated with carbon dioxide at 80°C until the pH was about 10.5, then the 40% treated green liquor was mixed with the remaining 60% of green liquor. The mixture was then treated with carbon dioxide at a reaction temperature of 80°C until the pH reached 9.5. In that situation, the particle size reached 14.11 μm . Compared with the one-step process, the particle size of silica generated by the seeding process was bigger and the sedimentation performance was improved.

Application: Silicon removal from green liquor of wheat straw soda pulping with carbon dioxide acidification by a one-step process or a seeding process might mitigate the problems of silicon in the chemical recovery system and improve the recycling of lime mud.

Because of the shortage of wood resources, nonwood materials such as wheat straw, reed, and bamboo are still used for papermaking in Europe and Asia. However, these nonwood raw materials contain up to 6% silicon, which will react with sodium hydroxide in the cooking process, form sodium silicate, and dissolve in black liquor. The silicate causes serious problems of scaling in the evaporators in which the black liquor is concentrated, and the evaporating efficiency decreases [1]. In the process of causticizing, 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]. No commercial process currently is available to remove the silicates. Burying or stock-piling lime mud with high silicon content both pollutes the environment and wastes chemicals.

Many researchers have studied the problems caused by silicon. Folke and Guerra [3] investigated two-step causticizing to remove silicon from green liquor in bamboo pulping. The silicon was selectively precipitated in the first step by adding 30% of the causticizing lime, 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 causticizing. About 56% of silicon was removed by the first step. However, about 44% of silicon was left in the lime mud generated in the second step. 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. Because of the high silicon content in the epidermis of straw resources, Chute [6] studied the means of removing silicon by pretreating the raw material with caustic soda. Almost all silicon in the epidermis was removed, but the internal silicon remained. Wang [7] investigated the method of silicon removal by adding aluminum oxide to green liquor to convert sodium silicate into aluminium silicate, which was filtrated out of the solution. Only 54.8% of the silicon was removed, so the lime mud could not be calcined for recycling. Consequently, there has been no effective process to remove the silicate from the green liquor.

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.

EXPERIMENTAL

Materials

For these experiments, green liquor from wheat straw soda pulping was collected from Aohui Paper Industry Co. Ltd. in Xi'an, Shaanxi Province, China, and carbon dioxide was provided by Shenkai Gas Co. Ltd., Shanghai, China.

One-step and seeding processes

Two processes were compared. In the one-step process, carbon dioxide was introduced into 200 mL green liquor with stirring. In the seeding process, 80 mL of green liquor was treated with carbon dioxide until the pH was about 10.5 to generate primary silica particles. Then the green liquor containing primary silica particles was mixed (seeded) with the remaining 120 mL of green liquor. The carbon dioxide continued flowing to the mixed green liquor to make the silicon precipitate on the surface of the primary silica particles and aggregate into secondary particles. For both processes, the effect of pH and reaction temperature on total silicon removal, particle size, and sedimentation performance of silica were investigated.

Determination of silicon content

The content of silicon in liquor was measured with spectrophotometry [8]. In weak acidic solutions, silicon reacts with a complex agent of ammonium molybdate to form silicon-molybdate ligand, and then the silicon-molybdate ligand is 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 determined with the spectrophotometer at 680 nm, and the silicon content was obtained by colorimetric analysis. The chemical equations and computational formula in colorimetric analysis were as follows:

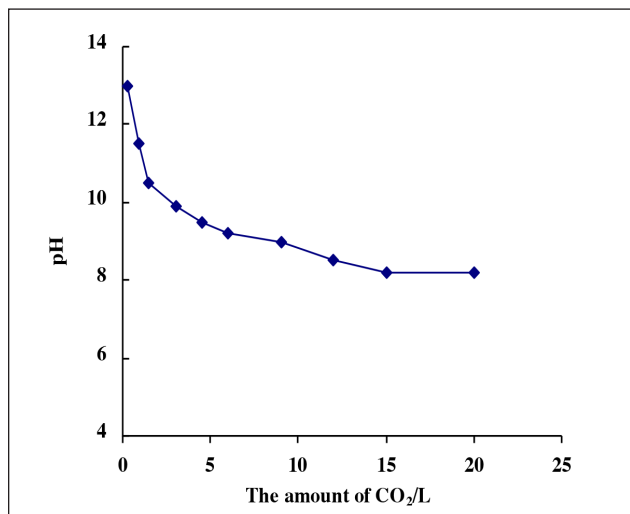


$$Y = 0.924x - 0.1731 \quad (R^2 = 0.9914) \quad (3)$$

in which Y and x represent the silicon content and the absorbance of $H_8[SiMo_2O_5(Mo_2O_7)_5]$ in green liquor, respectively.

Determination of particle size, sedimentation, and drainability

The particle size of silica was analyzed with a laser particle size analyzer.



1. Effect of the amount of carbon dioxide on pH of green liquor.

To determine sedimentation, the 200 mL green liquor containing silica particles was put into a 250 mL measuring cylinder, shaken well, and the cylinder was placed upright. The interface height of the precipitate was recorded at a certain interval. Within a certain standing time, the faster the interface height decreases, the better the sedimentation performance of the silica particle.

Drainability was evaluated by drainage rate test. A 200 mL suspension containing silica particles was filtered by Buchner funnel and the time needed to collect 150 mL filtrate was recorded.

RESULTS AND DISCUSSION

Analysis of green liquor

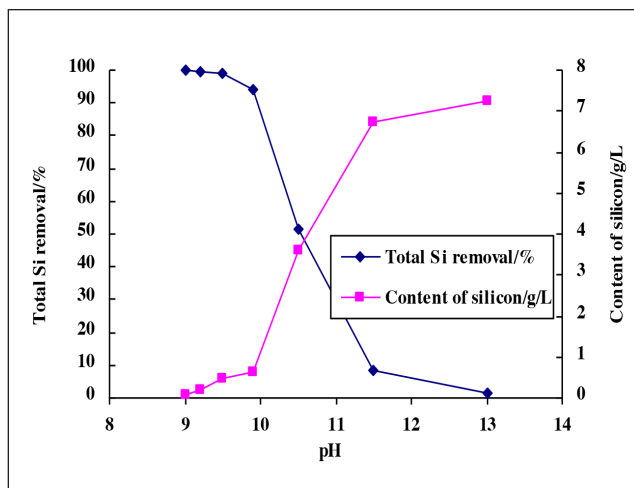
The composition of the green liquor was analyzed with inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Table I). The silicon dioxide content was 7.4 g/L, which will cause serious problems in the recycling of lime mud.

Effect of carbon dioxide on green liquor pH

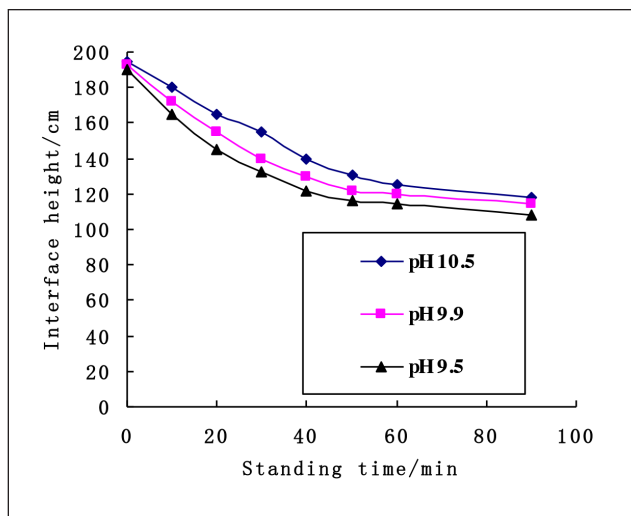
Carbon dioxide was flowed into the green liquor at room temperature and the alkali of the green liquor was neutralized. Figure 1 shows the effect of the amount of carbon dioxide on green liquor pH. The pH of green liquor decreased with increasing amounts of carbon dioxide, and it became stable at 8.2 after 15 L carbon dioxide was added.

One-step process: effect of pH on silicon removal

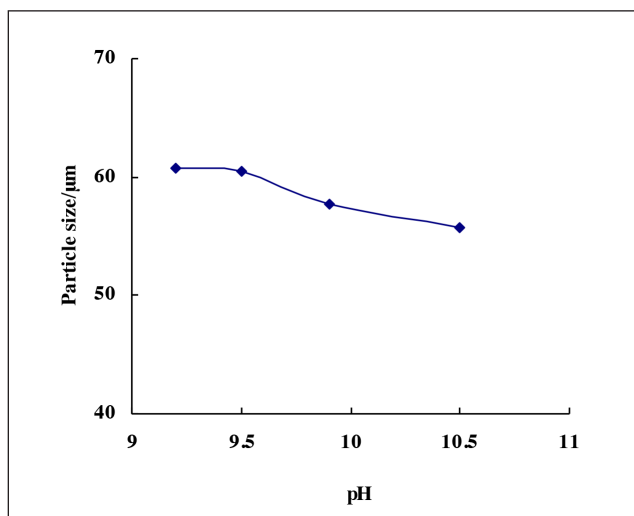
The silicon in green liquor was reacted when the carbon dioxide was flowed in with a speed of 0.3 L/min at room tem-



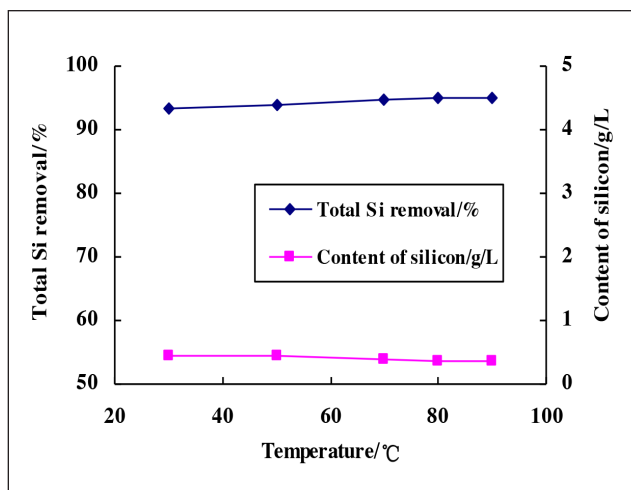
2. Effect of pH on silicon removal.



4. Effect of pH on sedimentation performance.



3. Effect of pH on the particle size of silica.



5. Effect of temperature on silicon removal.

perature. **Figure 2** shows the effect of pH on silicon removal. The content of silicon decreased with decreasing pH (i.e., the silicon removal improved). The content of silicon reduced to 0.6 g/L and about 93% of silicon was achieved when the pH was 9.2. The removal of silicon increased slowly as carbon dioxide was added continuously. When the pH decreased to 9.2, most of the silicon in the green liquor was converted to separable silica particles and about 99% of silicon was reacted.

Figure 3 shows the effect of pH on the particle size of silica at room temperature. The particle size increased slowly as the pH decreased, but showed no obvious change after the pH decreased to 9.5.

Figure 4 shows the effect of pH on sedimentation performance of silica particles generated at room temperature. The interface height of suspension decreased when the pH decreased from 10.5 to 9.5 with the same standing time. Therefore, the sedimentation performance was improved with decreasing pH. At the beginning of sedimentation, the

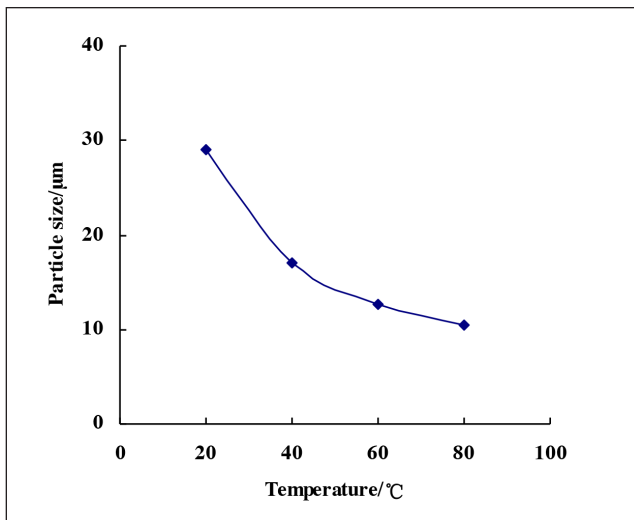
interface height decreased, but no obvious changes were observed after about 60 min.

These results demonstrate that silicon removal improved as the green liquor pH decreased. About 99% of silicon was removed when the pH reached 9.2 at room temperature. In addition, the sedimentation performance was improved and the particle size of silica increased gradually with decreasing pH of green liquor.

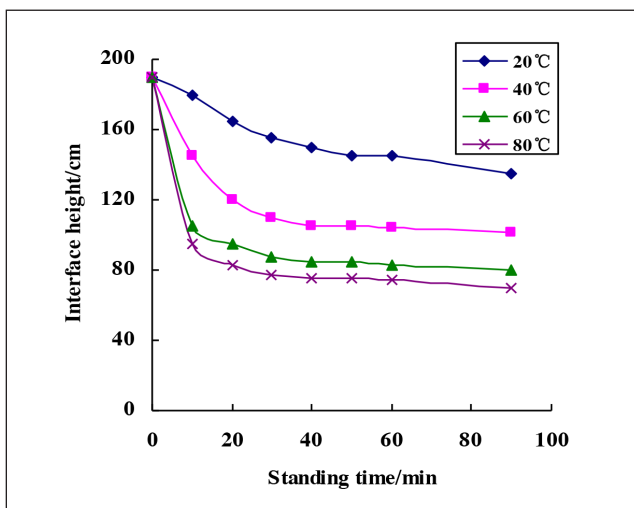
Effect of reaction temperature on silicon removal

The influence of reaction temperature on silicon removal was investigated as the carbon dioxide was flowed in with a speed of 0.3 L/min and reaction time was fixed within 15 min.

Figure 5 shows that about 93.5% of the silicon was removed when the temperature was 30°C. The silicon removal improved slightly at increasingly higher temperatures. When the temperature was 50°C and 90°C, about 93.9% and 95.0% of silicon was removed, respectively. This suggested that the



6. Effect of reaction temperature on the particle size of silica.



7. Effect of reaction temperature on sedimentation performance.

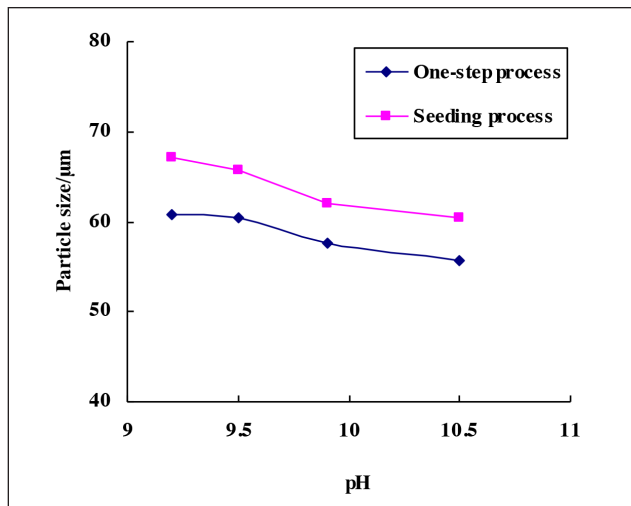
Temperature, °C	20	40	60	80
Drainage time, s	195	130	90	62

II. The effect of reaction temperature on drainability of silica.

reaction temperature did not have a significant effect on the silicon removal.

Figure 6 shows the influence of reaction temperature on the particle size of silica. The particle size apparently decreased with the reaction temperature increasing, which indicated that the higher reaction temperature influenced the growth of the silica particles negatively. This is because the surface tension of the particles decreased and the nucleation rate increased as the reaction temperature increased. In addition, more crystal nuclei were formed and the growth time of the silica particles was shortened. As a result, the particle size of silica became smaller [9].

After the green liquor was treated with carbon dioxide in



8. Effect of pH on the particle size of silica.

the one-step process at different temperatures, the sedimentation performance of silica particles was investigated (**Fig. 7**). The interface height decreased when the reaction temperature increased from 20°C to 80°C with the same standing time. The standing time was 60 min; the interface height was 145 cm with a reaction temperature of 20°C; and the interface height was 74 cm with a reaction temperature of 80°C. The sedimentation performance improved as reaction temperature increased.

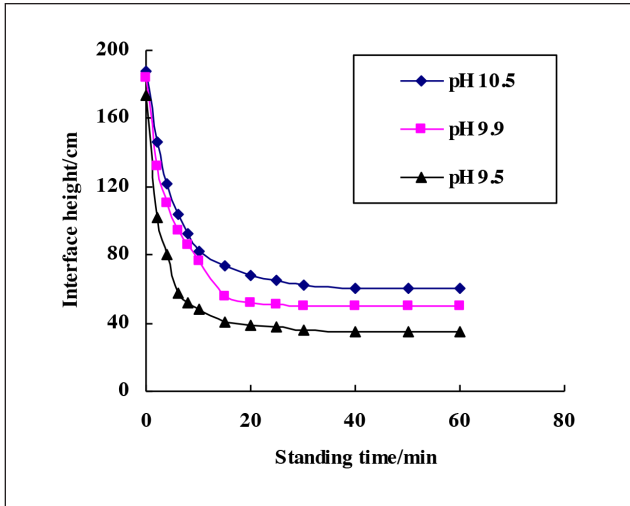
Overall, the reaction temperature had little effect on silicon removal, but it had a significant effect on the particle size and sedimentation performance of silica particles. The particle size decreased and the sedimentation performance increased rapidly as the reaction temperature increased.

Effect of reaction temperature on drainability of silica

After the green liquor was treated with carbon dioxide by the one-step process at different temperatures, the drainability of silica particles was measured; **Table II** shows the results. The drainage rate increased with the reaction temperature increasing. The drainage time was shortened from 195 s to 62 s when the temperature was increased from 20°C to 80°C. This was because the viscosity of green liquor decreased as the reaction temperature increased.

Seeding process: effect of pH on silicon removal

Silicon removal by the seeding process was carried out with a reaction temperature of 80°C. The particle size of silica generated under different pH in the second step was measured (**Fig. 8**). The particle size increased gradually as the pH of the green liquor decreased. Compared with the one-step process, the particle size generated by the seeding process was about 10% bigger under the same reaction conditions. This indicated that the seeding process aided the growth of silica particles.



9. Effect of pH on sedimentation performance.

Figure 9 shows the effect of pH on the sedimentation performance of silica particles by seeding process. As seen in Fig. 9, pH greatly influenced sedimentation performance. The interface height decreased when pH decreased from 10.5 to 9.5 with the same standing time. At the beginning of sedimentation, the interface height decreased quickly; no obvious changes were observed after about 20 min. Compared with the one-step process, the sedimentation time was shortened, so the sedimentation performance was improved by the seeding process.

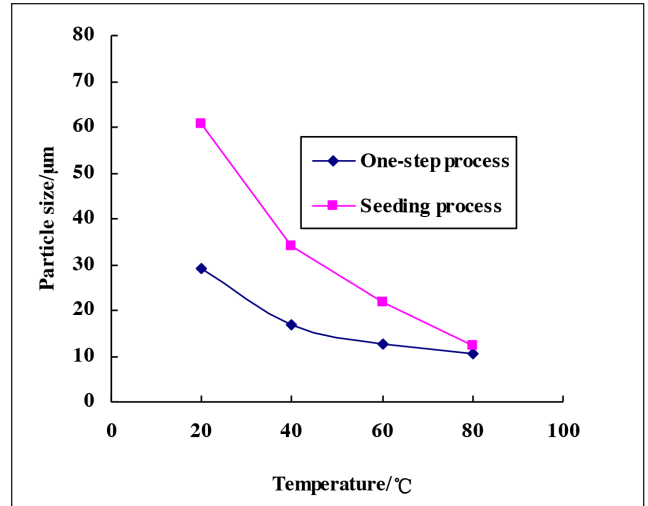
The particle size of silica generated by the seeding process was greater than that generated by the one-step process. With the decreasing of the pH in the second step, the particle size of silica increased and the sedimentation performance was improved.

Effect of reaction temperature on silicon removal

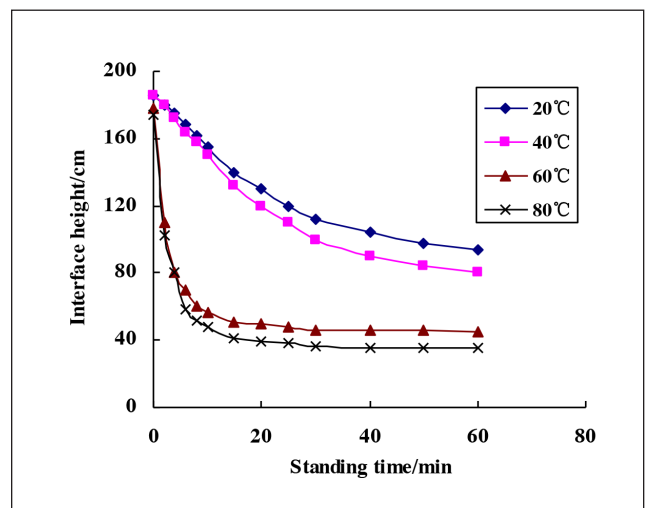
Figure 10 shows the influence of reaction temperature on the particle size of silica. The particle size decreased greatly as the reaction temperature increased. Compared with the one-step process, the particle size was apparently bigger in the seeding process, demonstrating that the seeding process was helpful to the growth of silicon particles.

After the green liquor was treated with carbon dioxide by the seeding process at different temperatures, the sedimentation performance of silica particles was investigated (**Figure 11**). The interface height decreased when the reaction temperature increased from 20°C to 80°C, indicating that the reaction temperature had a significant effect on sedimentation performance. Compared with the one-step process, the sedimentation time was shortened, so the sedimentation performance was improved by the seeding process.

The particle size of silica decreased and the sedimentation performance was improved significantly with the increases in reaction temperature. Compared with the one-step pro-



10. Effect of reaction temperature on the particle size of silica.



11. Effect of reaction temperature on sedimentation performance.

Temperature, °C	20	40	60	80
Drainage time, s	130	70	56	52

III. The effect of reaction temperature on drainability of silica.

cess, the sedimentation time was shortened, and thus the sedimentation performance was improved greatly by seeding processing.

Effect of reaction temperature on drainability of silica

After the green liquor was treated with carbon dioxide by the seeding process at different temperatures, the drainability of silica particles was measured. **Table III** shows the results. The drainage rate increased gradually as the reaction temperature increased. The drainage time was shortened from 130 s to 52 s when the temperature was increased from 20°C

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to 80°C. Compared with the one-step process, the drainage time was shortened, especially at lower temperatures.

CONCLUSIONS

The experiments described in this report led to the following conclusions:

1. The reaction temperature did not have a significant effect on the removal of silicon; however, the removal of silicon improved with decreasing pH. About 99% of the silicon was removed when the pH reached 9.2 at room temperature.

2. In the one-step process, the particle size of silica increased and the sedimentation performance was improved with the pH decreasing. As the particle size decreased, the sedimentation performance improved significantly as the reaction temperature increased. When the pH was 9.5 and reaction temperature was 80°C, the particle size of silica was 10.43 µm.

3. In the seeding process, the particle size was 14.11 µm with the same pH of 9.5 and temperature of 80°C as the one-step process. Compared with one-step process, the particle size of silica generated by the seeding process was bigger and the sedimentation performance was improved. The seeding process was helpful to the growth of silica particles and could improve drainability significantly. **TJ**

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ABOUT THE AUTHORS

We chose this topic to research because many mills with straw pulping face problems caused by high silicon content of green liquor in the chemical recovery process. Previous research was mainly based on the process of two-step causticizing to remove silicon from green liquor. However, only about 50% of silicon was removed by this process.

In this study, the green liquor was treated with carbon dioxide to precipitate silicon by one-step and seeding processes, and about 99% of silicon was removed. The most difficult aspect of this research was to find out the relationship between the particle size of silica, sedimentation performance, and reaction conditions. In the seeding process, 40% of green liquor was treated with carbon dioxide at 80°C until the pH was about 10.5, and then mixed with the remaining 60% green liquor, and finally, the mixture was treated with carbon dioxide at a reaction temperature of 80°C until the pH reached 9.5. As a result, the particle size was bigger and the sedimentation performance was improved.

Mills could use this method to mitigate the prob-



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lems of silicon in the chemical recovery system and improve the recycling of lime mud. Our next step is to find an industry partner to help with a pilot scale trial and then develop a method to remove silicon from green liquor of straw pulping.

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