

# Impact of Causticizing Calcium Carbonate from Soda Pulping of Wheat Straw on AKD Sizing

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The causticizing calcium carbonate (CCC) produced in the causticizing stage of the chemical recovery process in alkaline pulping of wheat straw has a high silicate content and is difficult to convert to calcium oxide in the lime kiln. The CCC can be utilized as a paper filler to avoid costly lime re-burning, but the silicate content of the CCC can have a negative impact on the wet-end chemistry of the papermaking process. In this paper, the effect of the silicate content of the CCC filler on AKD sizing was investigated. CCC fillers of various silicate contents were prepared in the lab by causticizing green liquor from the soda pulping of wheat straw and were added to fiber suspensions at the wet end of the papermaking process. The results show that the impact of the CCC filler on AKD sizing was associated with its silicate content. As the silicate content increased, the specific surface area and negative charge density of the CCC particles markedly increased, resulting in more AKD adsorption onto the CCC particles instead of fibers.

*Keywords:* Causticizing calcium carbonate; Silicate; Silica; Straw soda pulping; AKD sizing; Specific surface area; Charge density

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## INTRODUCTION

Causticizing calcium carbonate (CCC), also known as “lime sludge” or “lime mud,” is a byproduct of the causticizing stage of the chemical recovery process in alkaline pulping. In the alkaline pulping of wood materials, CCC is calcined in a rotary lime-kiln to produce quicklime to causticize the green liquor. However, in the alkaline pulping of non-wood materials, calcination of CCC is inefficient and costly as a result of silicate interference. In many of these cases, CCC is disposed of in landfills (Tang and Liu 2003).

Efforts have been made to eliminate the interference of silicates with the chemical recovery process of alkaline pulping. Silicates can be removed from the system by introducing carbon dioxide (CO<sub>2</sub>) into the black liquor, converting soluble sodium silicate into silica particles which can be separated from the black liquor by sedimentation (Myreen 1998; 2001). Using this process, about 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. Rao *et al.* (1998) studied a two-stage causticizing process wherein silicates were selectively precipitated out as calcium silicate in the first stage and purged from the system. However, the selectivity of the process was unsatisfactory. Chute and Vichnevsky (2008) studied the method of removing silica by pretreating the raw material with sodium hydroxide. They found that most silica in the epidermis could be removed by the caustic treatment, but the silica inside the material was less affected. Bohmer (1984) proposed

adding sodium aluminate or bauxite to green liquor to precipitate the silica as zeolite. High silica removal efficiency was claimed, but the process was too expensive to find any commercial applications. Wang *et al.* (2003) investigated the method of silicon removal by adding aluminum oxide to green liquor to convert sodium silicate into aluminum silicate, which was filtered out from the solution. About half of the silicon was removed, but the lime mud calcination issue remained. Silicates may be deposited onto pulp fibers to be purged from the system (Tutus *et al.* 2003). Unfortunately, this causes decreased pulp strength and silicate scaling on equipment.

It has been shown that the CCC from wood pulping may be used as a paper filler (Nanri *et al.* 2008). However, it has been reported that the CCC from non-wood pulping has a negative effect on AKD sizing (Raymond *et al.* 2004; Wang *et al.* 2014). Su *et al.* (2013) also reported that the acid-insoluble matter in the lime mud from straw pulping was the cause of the decreased AKD sizing performance. However, little has been reported in the literature on the effects of silicates on the physical and chemical properties of CCC, which in turn affect AKD sizing during the papermaking process.

In the current study, to understand how the physical and chemical properties of CCC are affected by silicates, CCC of various silicate contents was synthesized in the lab by causticizing partially de-silicized green liquor from wheat straw pulping with calcium hydroxide. The obtained CCC fillers of various silicate contents were added to pulp fiber suspensions at the wet-end of the papermaking process to examine their effect on AKD sizing performance. The CCC particles were observed with a scanning electron microscope (SEM), and their specific surface area and particle charge density were determined.

## EXPERIMENTAL

### Materials

Calcium oxide was from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and AKD emulsion (15% solid) from Kemira. CPAM (P63) and bentonite (Hydrocol O) were provided by Ciba Sweden. Green liquor from wheat straw soda pulping was obtained from Cailun Paper Co., Ltd., Xi'an, Shaanxi Province, China. The total alkali, active alkali, and sodium carbonate of the green liquor were determined according to TAPPI standard methods (T6240S-68), and the silicate content was determined by a spectroscopic method (Tong *et al.* 2005). The testing results of the green liquor are shown in Table 1.

**Table 1.** Composition of Green Liquor from Wheat Straw Pulping

Composition	Total Alkali (as NaOH)	Active Alkali (as NaOH)	Sodium Carbonate	Silicon Dioxide
Content (g/L)	115.07	20.67	125.08	7.02

### Desilication of the Green Liquor

The green liquor was desilicized by the one-step carbon dioxide precipitation method reported earlier (Xia *et al.* 2013). Then the desilicized green liquor was mixed with the original green liquor proportionally to generate green liquor samples of various silicate contents for the subsequent CCC preparation experiments.

## Preparation of CCC

In a 500-mL flask, 10 g of quicklime was mixed with 90 g of distilled water at 80 °C for 20 min. Then, 138 mL of green liquor with the desired silicate content was added gradually *via* a pipette into the flask at a rate of 0.055 mL/s. The contents were reacted for 2 h at 80 °C under continuous mixing at 300 rpm. The obtained CCC was filtered with Waterman No. 2 filter paper, washed with deionized water to neutral pH, and air-dried.

## Characterization of the CCC

The morphology of the CCC particles was examined with an FEI (USA) Quanta 200 scanning electron microscope (SEM), and the specific surface area was measured with a Micromeritics (USA) Gemini VII surface area analyzer. The charge density of the CCC particles was tested with a Müttek (Germany) PCD03 particle charge detector.

## Handsheet Preparation and Testing

A total of 0.2% AKD sizing agent (as the solid mass of the AKD emulsion), 20% CCC as filler, and 0.05% CPAM (0.1% water solution)/0.2% (0.5% water dispersion) bentonite as retention and drainage agents were sequentially added, while mixing, to a hardwood bleached kraft pulp (HBKP) of 425 mL Canadian standard freeness. All the chemical dosages were as solid mass percentages based on pulp fibers. Laboratory paper sheets (handsheets) were formed with a sheet former. The sizing degree of the lab paper sheets was tested according to TAPPI T441 om-13 (2013).

## Adsorption of AKD by the CCC Particles

The amount of AKD adsorbed by the CCC particles was determined using the UV spectrophotometry in two steps (Wang *et al.* 2014). In the first step, the absorbance of AKD at various concentrations was determined at the wavelength of 238 nm to obtain a calibration curve, as shown in Fig. 1.

In the second step, 0.1 g of AKD was mixed with 10 g of CCC suspended in 100 mL of water for 5 min. The mixture was then centrifuged for 10 min at 3000 rpm. The absorbance of the supernatant was determined at the wavelength of 238 nm. The content of AKD in the supernatant was calculated using the established calibration curve. The amount of AKD adsorbed by the CCC particles was calculated by subtracting the amount of AKD in the supernatant from the total amount of AKD added.

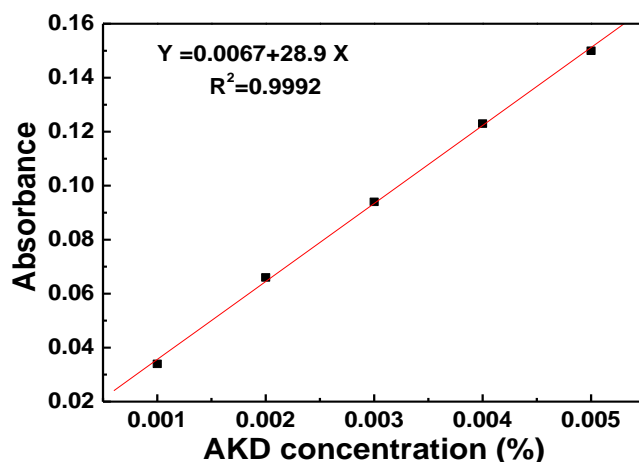


Fig. 1. The absorbance-concentration calibration curve for AKD solutions

## RESULTS AND DISCUSSION

### Effect of CCC's Silicate Content (as silica) on AKD

The effect of the CCC of different silicate contents on AKD sizing performance is shown in Fig. 2. It should be noted that the dosages of CCC and AKD were fixed at 20% and 0.2%, respectively, in all cases. The sizing degree was evaluated as the Cobb value, an indication of the amount of water absorbed by the paper. A lower Cobb value indicates better sizing, and a higher Cobb value indicates poorer sizing.

Figure 2 shows that with decreasing CCC silicate content, the Cobb value quickly decreased, indicating improved AKD sizing performance. When the silicate content of the CCC was 5.18% or higher, the Cobb value was higher than 45 g/m<sup>2</sup>, and the error bar of testing was wide, indicating that the sizing performance was poor and unstable. When the silicate content of the CCC was reduced from 5.18 to 3.20% (as silica), the Cobb value decreased from 46.5 to 27.7 g/m<sup>2</sup>. When the silicate content was further reduced to 0.31% (as silica), the Cobb value dropped to 25.9 g/m<sup>2</sup>. It is evident that the silicate content of the CCC filler particles had a significant impact on AKD sizing efficiency.

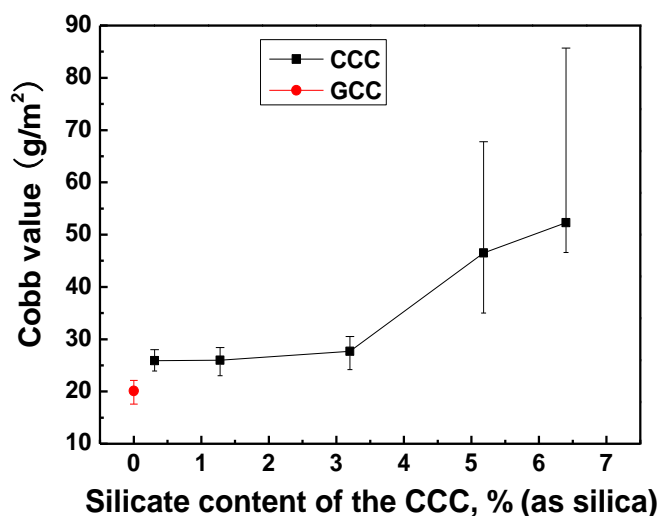
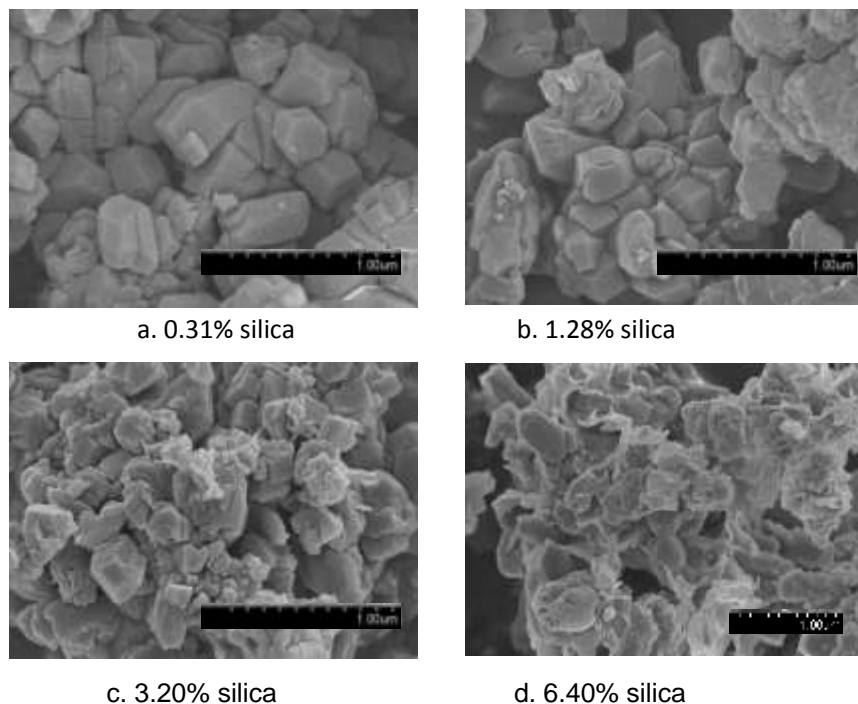


Fig. 2. Effect of the silicate content (as silica) of the CCC filler on paper sizing efficiency

### Effect of the Silicate Content on the Morphology of the CCC Particles

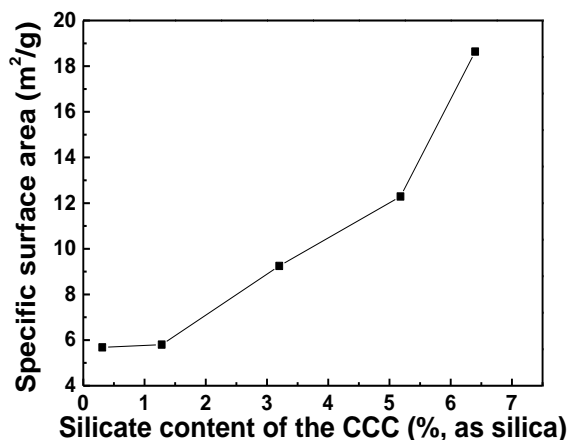
Figure 3 shows the morphology of CCC particles with various silicate contents. When the silicate content was low (0.31%, as silica), the CCC particles had a clear cubic crystal structure (Fig. 3a). The same was true at 1.28% silicate content (Fig. 3b). As the silicate content increased further to 3.20% (Fig. 3c), the CCC particles appeared to have amorphous materials on their surface, but the cubic calcite crystal shape could still be seen. When the silicate content increased to 6.40% (Fig. 3d), the cubic calcite crystal structure of the CCC particles was almost completely covered with amorphous material. The amorphous structure of the CCC particles provided more surface area for the adsorption of AKD, thus reducing the adsorption of AKD to fibers and lowering sizing efficiency (Colasurdo and Thorn 1992; Voutilainen 1996).



**Fig. 3.** SEM images of the CCC particles with various silicate contents (as silica)

### Specific Surface Area of the CCC Particles

The specific surface area of the CCC particles was tested using the low-temperature nitrogen adsorption method, the results of which are shown in Fig. 4. With increasing silicate content in the CCC samples, the specific surface area of the CCC particles increased markedly. When the silicate content was 0.31% (as silica), the specific surface area was 5.68 m<sup>2</sup>/g, and when the silicate content increased to 6.40% (as silica), the specific surface area increased by nearly 230%, to 18.64 m<sup>2</sup>/g. These results support the conclusion that higher silicate content in the green liquor resulted in CCC particles with substantially higher specific surface area, favoring the adsorption of AKD onto the CCC particles and reducing sizing efficiency. AKD adsorbed by filler particles of high specific surface area has much less access to the cellulose hydroxyl groups of fibers for sizing reactions (Bartz and Darroch 1994).



**Fig. 4.** Effect of the silicate content (as silica) on the specific surface area of the CCC particles

### Surface Charge Density of the CCC Particles

The surface charge density results are shown in Fig. 5. With increasing silicate content in the CCC particles, the negative charge density on the surface of the CCC particles increased markedly. When the silicate content was 0.31% (as silica), the negative charge density was -0.60 mmol/g; when the silicate content was 6.40% (as silica), the negative charge density increased to -1.94 mmol/g, an increment of nearly 240%. Positively charged AKD droplets adsorbed onto the negatively charged CCC particles *via* electrostatic attraction. For this reason, the CCC particles with stronger negative charge have larger AKD adsorption capacity (Lindström and Glad-Nordmark 2007).

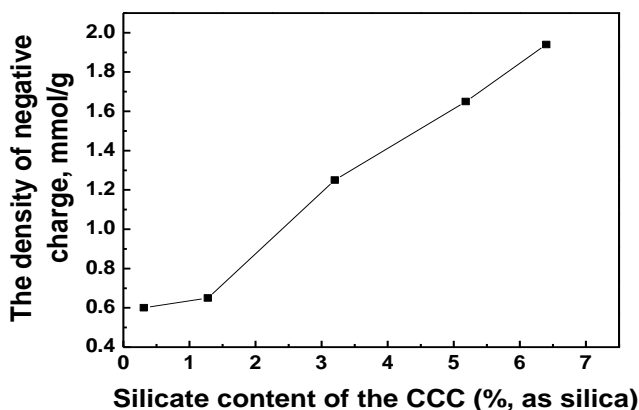


Fig. 5. Effect of the silicate content (as silica) on the charge density of the CCC particles

### Adsorption of AKD with CCC Particles

To show that the CCC particles with higher silicate content can adsorb more AKD in aqueous solution, a known amount of AKD was mixed with 10 g of the CCC particles suspended in 100 mL of water, and the amount of AKD absorbed by the CCC particles was determined by mass balance, as detailed in the experimental session. Figure 6 shows the amount of AKD adsorbed by the CCC particles at various silicate contents, as determined by UV spectrophotometry.

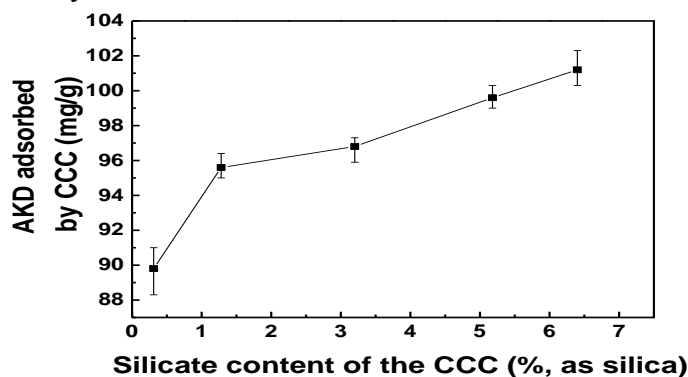


Fig. 6. Effect of the silicate content (as silica) of the CCC particles on AKD adsorption (by UV spectrophotometry)

It can be seen that with increasing silicate content of the CCC particles, the amount of AKD adsorbed by the particles increased. For example, when the silicate content was 0.31% (as silica), the amount of AKD adsorbed by the CCC particles was 89.8 mg/g, which increased to 101.2 mg/g when the silicate content was increased to 6.40% (as silica). It is well known that the amount of AKD adsorbed by the CCC particles contributed little to

sizing of the paper, and only AKD adsorbed onto cellulose fibers contributes to the sizing of paper (Voutilainen 1996; Karademir 2002).

## CONCLUSIONS

1. The silicates present in the green liquor from the alkaline pulping of non-wood materials had a strong effect on the physical and chemical properties of the resulting causticized calcium carbonate (CCC) particles, which in turn affected AKD sizing in the papermaking process to which the CCC was added as a paper filler.
2. The negative impact of the CCC on AKD sizing was found to be associated with its silicate content. AKD sizing efficiency decreased with increasing silicate content of the CCC.
3. SEM images revealed that the presence of silicates in the green liquor changed the morphology of the CCC particles significantly. When the silicate content of the CCC increased from 0.31 to 6.40% (as silica), the cubic crystal structure of the CCC calcite particles was almost completely covered with amorphous material most likely formed during the causticizing process from silicates in the green liquor.
4. The amorphous materials were porous and thus had larger surface area than the calcite crystals. As the silicate content increased, the specific surface area of the CCC particles increased more than threefold, from 5.68 to 18.64 m<sup>2</sup>/g.
5. As the silicate content of the CCC increased from 0.31 to 6.40% (as silica), the negative charge density of the CCC particles increased by more than 200%. As a result, more AKD sizing agent was adsorbed onto the CCC particles and less AKD was available for fiber sizing.

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