Further Understanding of the Silicon Morphological Fundamentals of Bamboo Culm

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Bamboo is one of the most important non-wood raw materials for the pulp and paper industry in Asia and particularly in China. However, its high silicon content can cause challenges in the pulping and alkali recovery systems. Further understanding of the distribution, morphology, and composition of silicon in bamboo culm will be beneficial in solving these challenges. In this study, modern analytical tools such as scanning electron microscopy (SEM) and scanning electron microscopy equipped with an energy dispersive X-ray (SEM-EDX) were used to characterize the distribution, morphology, and composition of silicon in the bamboo culm. The results showed that silicon is mainly distributed in the outer skin and inner skin. The silicon deposits exist in a number of shapes, and sinuate is the most common one. Their sizes range from about 0.15 μm to 0.9 μm in the cell wall and between 0.3 μm to 1.5 μm in the cell lumen. Localized silicon deposits are present in the forms of its oxide, silica, monatomic silicon, and/or organosilicon. Based on the above results, two potential techniques are recommended for pulp mills to minimize silicon-related challenges.

Keywords: Bamboo; Silicon; Distribution; Composition; Morphology

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INTRODUCTION

Bamboo (*Neosincalamus affinis*) is a fast growing and widespread plant in temperate, tropical, and subtropical regions. This versatile plant can be used for textile manufacturing, building materials, and even Chinese medicine (Zhang and Zhang 2000). Bamboo is also an important non-wood raw material that has been used in the pulp and paper industry in China (Zhao *et al*. 2010; Chen *et al*. 2016).

The high silicon content of bamboo can cause silicon problems in many aspects of pulp and paper manufacturing. In alkaline pulping processes, silicon in bamboo reacts with sodium hydroxide to form sodium silicate, which then enters the alkali recovery system along with the alkaline spent liquor. Sodium silicate increases the viscosity of the spent liquor, which leads to difficulties with spent liquor evaporation and increases the scaling on process equipment. In addition, smooth operations of typical pulp and paper processes such as raw material preparation, pulping, brown stock washing, and paper machine operation can be adversely affected. Therefore, it is important to lower the silicon intake to pulp mills. For this purpose, further knowledge of the content, distribution, morphology, and composition of silicon in bamboo culm is needed.

Biologically, silicon is essential for the growth of plants such as scouring rushes and grasses (Chen and Lewin 1969). Silicon enters plants as water-soluble monosilicic acid (H_4SiO_4), which is transported through the root, stem, and leaves (Barber and Shone 1966). Silicic acid becomes polymerized, resulting in the deposition of solid within or external to cells (Piperno 1985). The silicon deposits take the form of solid amorphous silica or silica gel (Kaufman *et al*. 1970; Conley 2002). It can be deposited as hairs (or trichomes) at stomata, in ordinary epidermal cells, and in specialized silica cells in grasses. It is particularly rich in vascular plants, including horsetails, grasses, and hemps (Kaufman *et al*. 1970).

The silicon content of terrestrial plants varies from 1% to several percent of the dry matter; some plants contain very high silicon contents of 10% or more (Epstein 1994). In the grass family, various shapes of silica have been observed and classified. Mulholland and Rapp (1992) divided the silicon deposits into eight shapes that are based on the contours of silica bodies. These shapes include the triangle, rectangle, pentagon, cross, sinuate, dumbbell, rondel, and saddle. Page (1992) classified them into the following six: pooid (festucoid), chloridoid, panicoid, elongate, fan-shaped, and point-shaped. The silicon concentration is particularly high in the roots and leaves of some plants. Alexander *et al*. (2003) performed a systematic study on the silicification of bamboo root and leaf. They found that the silicon deposition in leaves is in the epidermis cell and that the deposition of silicon in bamboo roots is only in endodermal cell walls. The silicon content in the root endodermal cell walls is even higher than in the outer leaf epidermal walls. The silicon content of bamboo shoots and leaves varies from 2.8% to 15.9% SiO_2 on a dry weight basis (Takahashi *et al*. 1981).

Due to the importance of bamboo as a key non-wood raw material for the pulp and paper industry in the southwest region of China, a large collaborative project funded by both the industry and the Chinese Government was initiated. The aim of this project was to improve the kraft pulping processes that use bamboo as the raw material. The results present in this paper are part of this initiative.

The focus of this study was to determine the distribution, morphology, and composition of silicon in bamboo culm by using modern analytical tools, including scanning electron microscopy (SEM) and scanning electron microscopy equipped with an energy dispersive X-ray (SEM-EDX). The results can be the first step towards decreasing silicon-related challenges in the kraft pulping processes.

EXPERIMENTAL

Material

The 2-year-old bamboo (*Neosincalamus affinis*) culms were obtained from Guizhou Chitianhua Paper Ltd., Tanson Group, Chishui, China. All culms were completely washed with purified water before sample preparation and analysis.

The cross section and tangential section with a thickness of approximately 1 mm were cut from fresh culm using a double-edge blade and then dried in an ambient environment for SEM and SEM-EDX analyses. Both the outer skin with a thickness of approximately 0.1 mm and the inner skin with a thickness of approximately 0.3 mm were cut from air-dried culm for ash content testing and ash sample preparation. The outer skin was cut with a small inclined angle of about 5° to the outer surface for SEM observation.

Determination of Ash Content and Preparation of Ash Sample

Samples of the outer skin, inner skin, and culm were oven-dried separately at 105 °C until a constant weight was reached. They were cooled for 30 min in a dehydrator with a drying agent prior to determining the dry weight.

Ash content was determined by placing a 2 g oven-dried sample in a pre-dried porcelain crucible in a furnace while gradually increasing the temperature, which charred the sample at 270 °C until no smoke was emitted. The temperature was then increased to 575 °C and maintained at that temperature for 4 h. The samples were cooled for 45 min in the dehydrator with a drying agent to determine the ash dry weight. Ash content was calculated using Eq. 1.

$$Ash = \frac{ash\ weight,\ g}{oven\ dried\ sample\ weight,\ g} \times 100\% \quad (1)$$

To avoid destroying their structure, the ash samples were carefully transferred and pasted on an aluminum base with conductive tape for SEM observation and SEM-EDX analysis.

SEM Observation and SEM-EDX Analysis

The samples of cross section, tangential section, outer skin, ash of outer skin, ash of inner skin, and ash of whole culm were pasted on an aluminum base with conductive tape and sputtered with a thin layer of gold for electrical conductivity. Both morphological observation and semi-quantitative elemental analysis of these samples were done using a S4800 scanning electron microscope (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray (EDX).

The SEM device was operated at 1.3×10^{-3} Pa and 3 kV for the cross section and tangential section and 5 kV for the outer skin, ash in outer skin, inner skin, and whole culm. SEM was operated at 20 kV for the semi-quantitative elemental analysis. The energy resolution of the EDX analysis was 123 eV. The error range due to the limitation of the instrument was approximately 1 to 2 wt.%.

RESULTS AND DISCUSSION

Anatomy

The bamboo culm consists of the rind, basic, and vascular systems (Fig. 1a). The rind system is made of the epidermis, hypodermis, and cortex. Near the inner surface is the "pith-ring", which is composed of approximately 9 layers of short and square cells (Fig. 1b); a previous study reported that the pith-ring is made of 8 to 15 layers of short and square thick-walled cells (Li *et al.* 1997).

As shown in Fig. 1c, there are numerous vascular bundles. The shape and size of these vascular bundles varies significantly from the rind towards the pith-ring. Those close to the rind are small, while those near the pith-ring are large.

Silicon Content and Distribution

The ash samples were subjected to EDX element analysis. As shown in Fig. 2, C, O, Na, Mg, Si, P, S, Cl, K, Ca, and Mn were present in the ash of the culm. K was the richest among those inorganic elements, followed by Si.

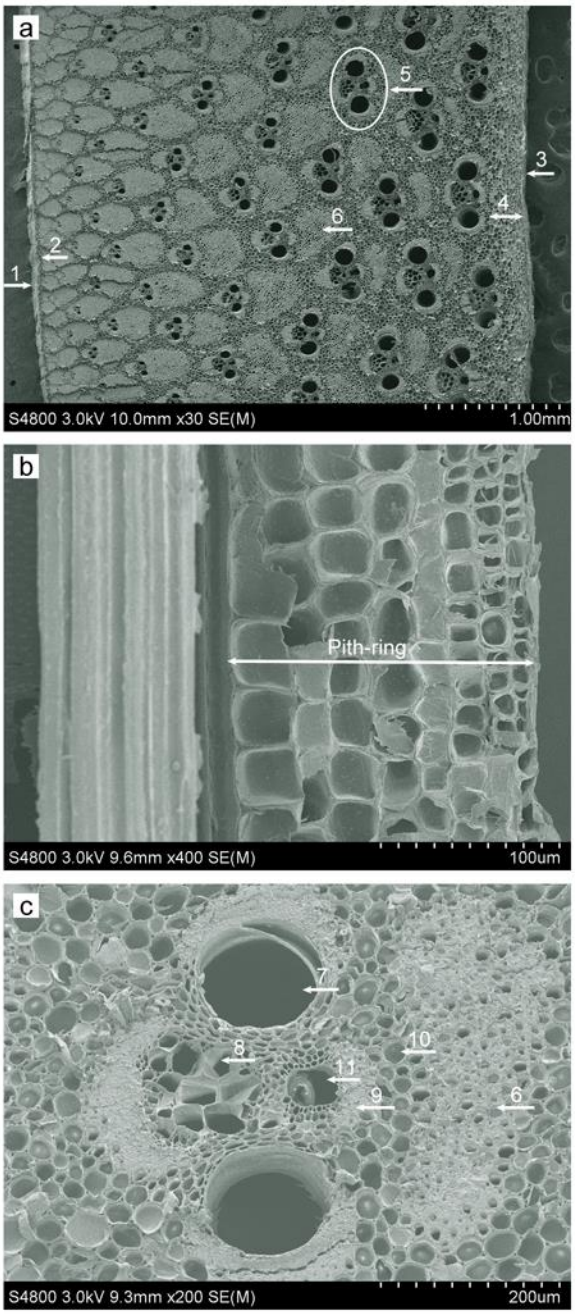
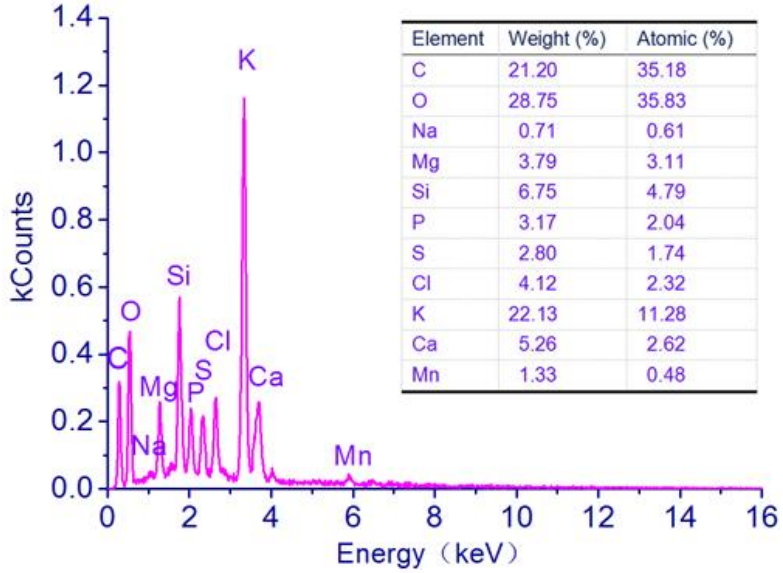


Fig. 1. SEM of bamboo culm (a) cross section: (1) outer surface; (2) rind system; (3) inner surface; (4) pith-ring; (5) vascular bundle; (6) fiber strand; (b) tangential section of pith-ring; and (c) vascular bundle: (7) metaxylem vessel; (8) phloem; (9) sclerenchyma sheath; (10) parenchyma cells; (11) intercellular space derived from protoxylem

Line scanning by SEM-EDX was carried out on the cross section (Fig. 3). Results showed that silicon was unevenly distributed, and the highest intensity of silicon distribution was in the area of rind and outer surface. This result matched well with the conclusions of Ryoya *et al*. (2015) that the culm of moso bamboo chips is covered with a hard multi-layered epidermis containing abundant silica cells.

Figure 3 also indicates that there were considerably high silicon distributions at the inner surface and localized silicon deposition in various positions of the cell. The results are consistent with the observation of Lanning *et al*. (1980) that silica is usually deposited in the cell walls and sometimes as bodies in the cell lumen.



Element	Weight (%)	Atomic (%)
C	21.20	35.18
O	28.75	35.83
Na	0.71	0.61
Mg	3.79	3.11
Si	6.75	4.79
P	3.17	2.04
S	2.80	1.74
Cl	4.12	2.32
K	22.13	11.28
Ca	5.26	2.62
Mn	1.33	0.48

Fig. 2. EDX spectrum of elementals in the ash of bamboo culm

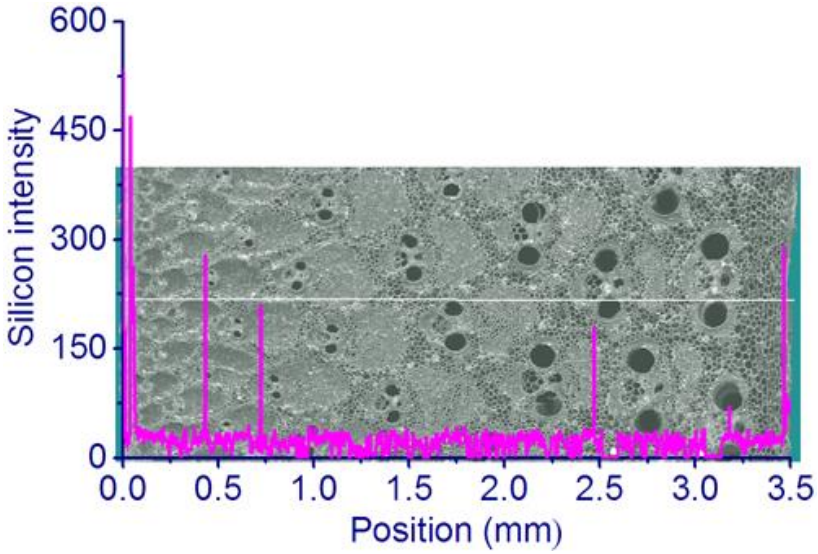


Fig. 3. Silicon distribution intensity along with the white line path on the cross section of bamboo culm (SEM-EDX line-scanning)

Figure 4 shows the results of ash and silicon content for the outer skin region (rind based), the inner skin region (pith-ring based), and the culm. The ash content in the outer and inner skin is much higher than that in the culm. Similarly, silicon content and distribution in the bamboo culm show the same trend as the ash content and distribution, which further supports the conclusion that higher silicon content localized on the outer and inner skin of bamboo culm.

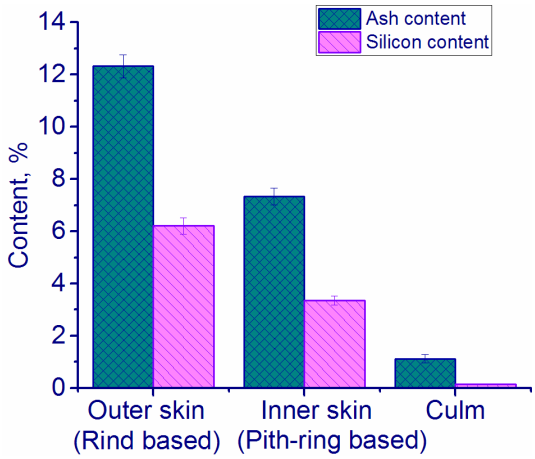


Fig. 4. Comparison of ash and silicon content at different positions of culm (Note: Silicon content (%) = Ash content (%) × Silicon weight (%) based on the results of SEM-EDX element analysis)

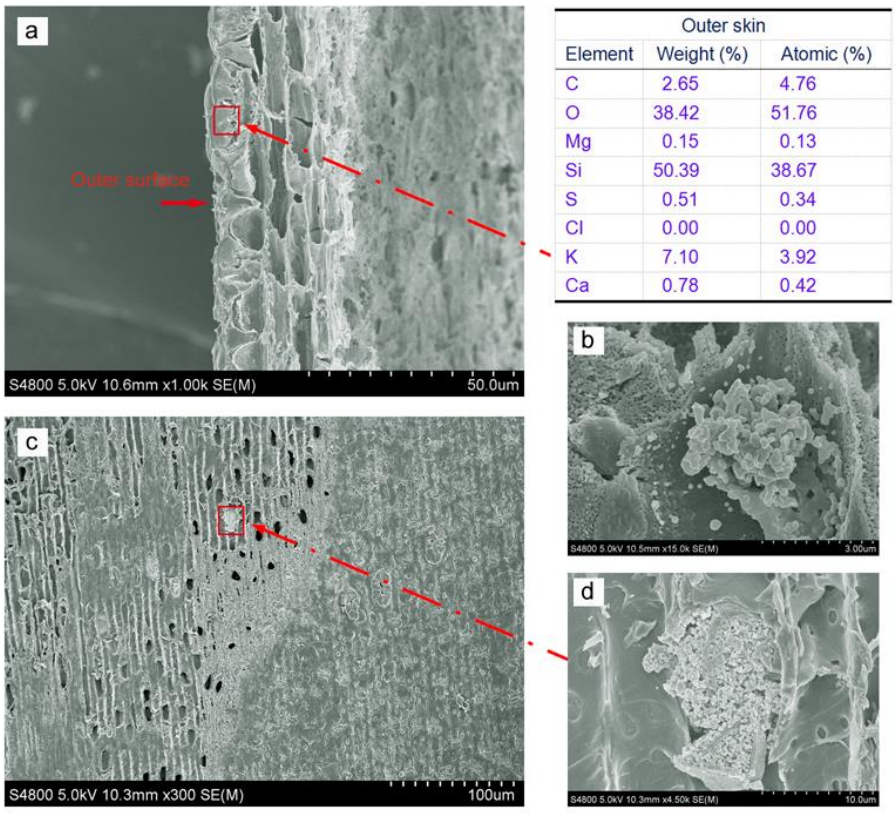
Silicon Morphology and Composition

Figure 5a shows the silicon distribution in the outer skin region. The ash content shows the same trend as the silicon distribution. The rich ash content of the outer skin is noticeable. Due to the high silicon concentration, the ash nearly maintains the intact morphology of the cells. The outer skin is composed of multi-layered silicon-containing cells. The outermost layer is either completely or almost filled by silicon, based on the results of SEM-EDX element analysis in the insert table.

The next layers also have a clear ash (silicon) frame (Fig. 5a), and most of these cells are empty in their lumen, although there are some silicon particles deposited in the cell lumen (Fig. 5b). The outer surface (cut at a significantly small angle) further confirms the localized silicon deposits in these cells (Fig. 5c and Fig. 5d).

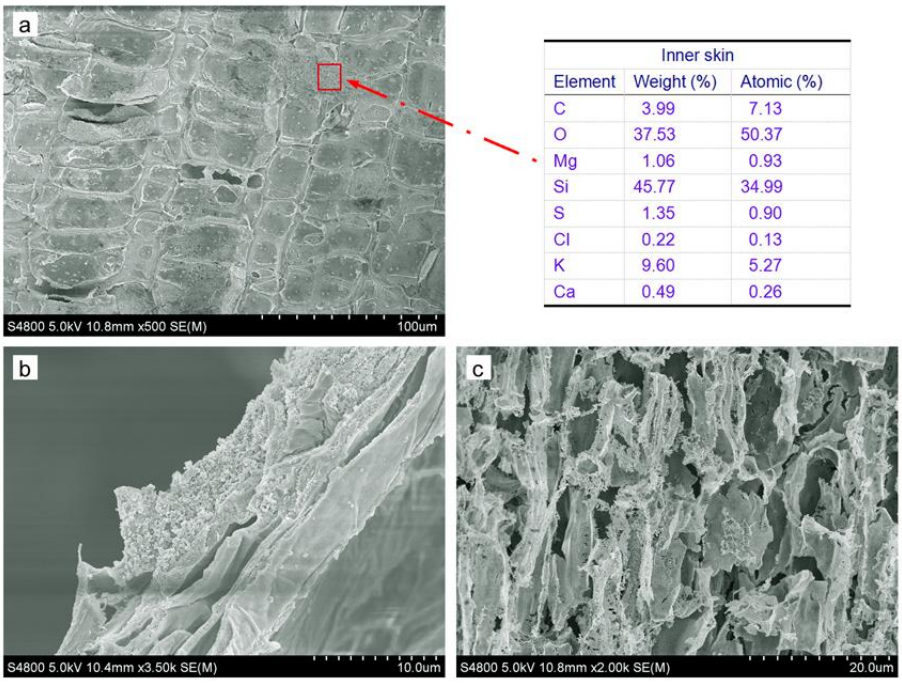
Triangle, rectangle, and oblong silicon-containing cells are found in the outer most cell layer (Fig. 5a). Triangle cells and oblong cells are about 8 to 13 μm in the radial direction of culm, 6 to 14 μm in the height direction, and are fully filled with silicon. Rectangle cells are about 11 to 13 μm in the radial direction, 18 to 30 μm in the height direction, and are partially filled with silicon in the outer most cell wall. In the outer skin region, the silicon frame in the cell wall is thick, gradually becoming thinner in the radial direction from the outer surface to the inner surface.

The silicon distribution and other related results of the inner skin are shown in Fig. 6. These results are somewhat different from those in the outer skin. In contrast to the thick-wall silicon frames (Fig. 5a), thin wall silicon frames are evident in the inner skin surface (Fig. 6b). The thickness of the silicon frame in the three layers of pith-ring cell closed inner surface is thicker than the inner most silicon layer. A number of silicon particles are deposited in the lumen of those cells. The silicon frame in the radial direction from the inner surface to outer surface begins thinning and eventually disappears (Fig. 6b and Fig. 6c). The SEM-EDX element analysis results in Figs. 5 and 6 also show that silicon is important in terms of both weight and atomic percentage. Jones and Milne (1963) stated that silicon is deposited or secreted as silica in epidermal cells and the cell wall. The atomic ratio of oxygen to silicon in SiO_2 is 2. However, the results shows that in the outer skin, the Si to O atomic ratio is 1.34 (Fig. 5), while in the inner skin, the Si to O atomic ratio is 1.44 (Fig. 6), both of which are lower than 2. Those indicate that in addition to silica (SiO_2), monatomic silicon and/or organosilicon could also have been present.



Outer skin		
Element	Weight (%)	Atomic (%)
C	2.65	4.76
O	38.42	51.76
Mg	0.15	0.13
Si	50.39	38.67
S	0.51	0.34
Cl	0.00	0.00
K	7.10	3.92
Ca	0.78	0.42

Fig. 5. (a) Silicon-based ash skeleton frame of the outer skin (rind based). (b) Silicon deposited particles in cell lumen; (c) Silicon deposited particles (Arrows) in the outer skin; (d) Deposited silicon particle in cell lumen



Inner skin		
Element	Weight (%)	Atomic (%)
C	3.99	7.13
O	37.53	50.37
Mg	1.06	0.93
Si	45.77	34.99
S	1.35	0.90
Cl	0.22	0.13
K	9.60	5.27
Ca	0.49	0.26

Fig. 6. Ash frame of the inner skin (pith-ring based). (a) Inner surface; (b) Section of inner skin ash frame; (c) Ash frame of inner skin adjacent to culm center

The silicon particles in cell walls exhibit a number of shapes, and almost cover the eight groups that Mulholland and Rapp (1992) reported (Fig. 7). Sinuate is the most frequent shape. The silicon particle sizes varies from 0.15 μm to 0.9 μm, which is much smaller than the silicon deposited particles on the outer and inner surfaces with varied sizes from 0.5 μm to 1.5 μm (Fig. 5b).

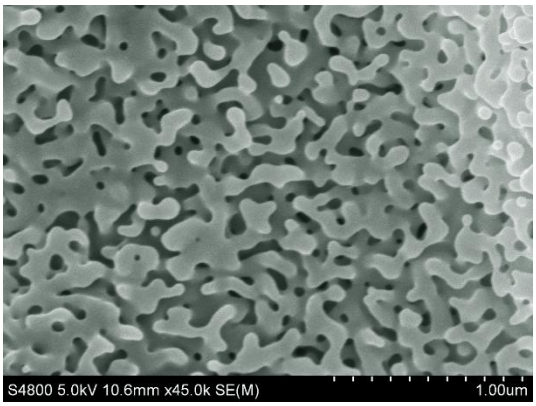


Fig. 7. Skeleton frame of silicon particles on the cell wall

The present study has shown that silicon is rich in the ash of *Neosincalamus affinis* culm. Other elements including C, O, Na, Mg, P, S, Cl, K, Ca, and Mn are identified using SEM-EDX semi-quantitative analysis. The localized silicon is highly concentrated in the outer surface and rind (6.21 wt.%), inner surface (3.36 wt.%), and some of cell lumen (Figs. 2, 3, 4, 5, and 6). These localized silicon deposits have a variety of shapes, and the size and thickness of the silicon wall changes at different positions.

There is no doubt that silicon particles in the cell wall are surrounded by an organic substance. SEM-EDX semi-quantitative analysis indicates that silicon exists in bamboo culm in the form of its oxide, amorphous silica, and monatomic silicon and/or organosilicon. These components are easily dissolved in pulping alkali liquor to form sodium silicate, which could form insoluble complexes with metallic oxide or salts such as CaO, MgO, Al_2O_3, and $AlCl_3$ (Park and Englezos 1998; Xu *et al*. 2013).

These results suggest some practical solutions. The most direct way is to decrease the silica intake to the pulping system by removing the silica rich components (outer surface, rind, and inner surface) during the preparation of raw materials. For this direct way, additional investments, such as debarking and/or depithing, should be included to remove the silica-rich components during the stock preparation, which will also decrease the overall pulp yield. However, some metallic compounds (*e.g*., sodium aluminate) could be added to the pulping system. The objective is to form insoluble silicon-aluminum complexes so that silicon dissolution is minimized in the pulping process.

Once sodium silicate is formed from the silicon and alkali contact, the metallic compound immediately reacts with sodium silicate, which covers cell or silicon particle surfaces and holds back or slows down the silicon dissolution into the bulk of black liquid. The Si-Al complexes are deposited onto the fiber wall/lumen so that the silicon content in pulping spent liquor is lowered. Future studies will be required to determine if this method is practicable.

CONCLUSIONS

1. Two silicon-rich regions in the outer skin and inner skin are identified, while some silicon particles are also deposited in the lumen.
2. Three types of silicon cells form a compact outermost cell layer in the outer skin, with full or almost full silicon filling and silicon in the bamboo culm, which exists in the form of its oxide, amorphous silica, and monatomic silicon and/or organosilicon.
3. Silicon frame in the cell wall is the thickest in the outer most cell wall and becomes thinner along the radial direction from the outer surface to the inner surface and finally disappears.
4. The silicon particles that make up the structure of silicon-containing cell walls have a number of shapes, with sinuate being the most frequent one. The size of silicon particles varies from about 0.15 to 0.9 μm in the cell wall and about 0.3 to 1.5 μm in the cell lumen, where they forms up to 20 micrometers of silicon deposited particles.
5. Based on the results obtained from this study related to the composition, structure, and distributions of silicon in *Neosincalamus affinis* culm, two potential techniques are recommended to the pulping system to minimize silicon-related challenges.

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