

MASS BALANCE OF SILICA IN STRAW FROM THE PERSPECTIVE OF SILICA REDUCTION IN STRAW PULP

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The high silica content of wheat straw is an important limiting factor for straw pulping. High silica content complicates processing and black liquor recovery, wears out factory installations, and lowers paper quality. Each section of wheat straw has different cells and chemical compositions and thus different silica content. In this work, the silica content of balled straw samples were examined according to their physical components, including internodes, nodes, leaves (sheath and blade), rachis, grain, other plant bodies, and other plant spikes. Mass distribution of silica was determined by a dry ashing method. Half (50.90%) of the silica comes from leaves, and its mechanical separation will reduce the silica content in wheat straw pulp significantly. Destroying silica bodies by sonication will increase the strength properties of straw pulp.

Keywords: Wheat straw; Silica; Desilication; Ash; Phytolith

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INTRODUCTION

Wheat straw is the most widespread and easily available agricultural residue used for papermaking. Short fiber demand and high annual yields of pulp per hectare have encouraged the use of straw and other grasses as raw materials in the pulping industry (Atchison 1996; Pande 1998; Thykesson *et al.* 1998; Pahkala *et al.* 1999; Pahkala and Pihala 2000; Stern 2002). However, high silica content is a major limiting factor for straw pulping.

The silicon in living plants is present as three basic forms: insoluble silica, colloidal silicic acid, and silicate ions. Nearly 90% of the silicon in rice straw is stored as insoluble silica. Previously, X-ray diffraction studies of silica (body) deposits in plants revealed an amorphous pattern similar to opals, so they are frequently referred to as being biogenic opals (opalits) (Cheng and Kim 1989). The function of silica bodies is not understood clearly yet. However, they do cause wear in teeth of grazing animals (Cutler *et al.* 2008).

Wheat (*Triticum aestivum* L.) straw has various morphologies, and its chemical composition is dependent on genetics, location, and growth conditions. Carbohydrate contents vary by approximately $\pm 5\%$ (absolute), $\pm 2\%$ lignin, and $\pm 3\%$ ash. Silica and extractives include similar amounts (Mckean and Jacobs 1997). High silica content complicates processing and black liquor recovery (Blander and Pelton 1997), wears out factory installations, and lowers paper quality. Therefore, many scientists have published

numerous articles on the topic of pulp desilication (Pan *et al.* 1999; Abasolo *et al.* 2001; Tutus and Eroglu 2003; Hess *et al.* 2003; Pekarovic *et al.* 2006). Decreasing the silica content of raw materials from agricultural residues is important for the pulping industry.

The aim of this study is to determine the distribution of silica in baled agricultural straw residue from a wheat crop. The results will offer an idea about the preparation of the raw material for optimization of the pulping process with respect to the silica content of pulp.

EXPERIMENTAL

The wheat straw bale was acquired from the Central Anatolia region of Turkey. Industrial straw pulping processes do not involve any selective separation of the straw; therefore all components of the wheat straw bale are included in the investigation. One kilogram of randomly taken straw was separated manually by physical contents (internodes, nodes, leaves (sheath and blade), rachis, grain, other plant bodies, and other plant spikes). The moisture content of samples was determined according to the TAPPI T 264 test method.

There are different methods for determining the silica (acid insoluble ash) content in plants (Bone 2007). The goal of this study was to measure the insoluble silica content that contributes to the fiber rigidity and damages of factory installations. Fibers containing epidermal long cell phytoliths will be inflexible, and big insoluble opalites will wear equipment. Therefore, the morphological structure of the ignited test specimens was destroyed by sonication (ultrasound treatment) in liquid media. Silica contents of the separated samples were determined gravimetrically by the dry ashing method.

First, the plant material was cleaned by rinsing with distilled water (Wallis 2003). The clean sample was transferred to a nickel crucible, carbonized gently over a Bunsen burner, and reduced to ash in a muffle furnace at 500 °C for two days. The residue was then weighed as ash. The ash was treated with 15 mL of 3.5 N HCl in a glass tube and sonicated (38 kHz 250 W) at 20 °C for 10 min and then placed in a 70 °C water bath for 30 min (Parr *et al.* 2001). The sample was centrifuged for 5 min at 300 revs/min and decanted. The sample was rinsed with 30 mL of distilled water and decanted after centrifugation. The residual organic compounds were removed with peroxide treatment (Wallis 2003). After the addition of 30 mL of 15% H₂O₂, the sample was sonicated for 2 min and maintained at 70 °C via a water bath for 24 hours. The sample was centrifuged for 5 min at 300 revs/min and washed after decantation. Finally, the samples were reignited inside the muffle furnace at 500 °C for 6 hours, and the silica contents were determined. Ash and silica weight percentages were calculated according to the oven dry weight of straw.

A microscope slide was prepared by embedding silica in Canada balsam (Merck M101691) after staining with 0.5% malachite green. Images were collected with a Leica DM2500 microscope, processed with “ImageJ” software, and phytoliths were identified according to the method reported by Ball *et al.* (1996).

RESULTS AND DISCUSSION

The mass balance of wheat straw did not differ from previous investigations (Fig. 1) where only the node, internode, and leaf were considered. According to McKean and Jacobs (1997), the node content through the different cultivars varies by approximately 6%, and some variation was seen in the leaf and internode contents (McKean and Jacobs 1997). Mechanical harvesting of the grain breaks off some of the leaves. McKean and Jacobs (1997) also reported a decrease in leaf content after mechanical harvesting from 46% to 9%. The stated minimum leaf content of 9% is lower than the 26% reported by Ernst *et al.* (1960) and the 25.92% determined in this study. This data shows that the amount of leaves in straw can be reduced by mechanical processing during harvesting.

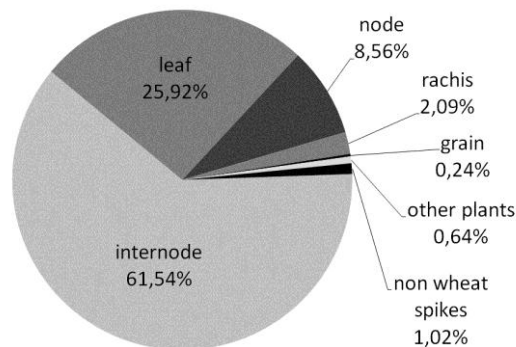


Fig. 1. Mass balance of wheat straw bale by physical content

The ash (9.51%) and silica (4.35%) content determined in this study (Fig. 2) are similar to the results obtained by McKean and Jacobs (1997). They reported 5.7 to 9.1%, 8.6 to 13.1%, and 8.7 to 15.1% ash, and 1.9 to 4.2%, 1.2 to 4%, and 4.8 to 11.7% acid insoluble ash for internodes, nodes, and leaves, respectively. Hess *et al.* (2003) determined similar ash content for some of the varieties, but the silica content was quite low for all varieties.

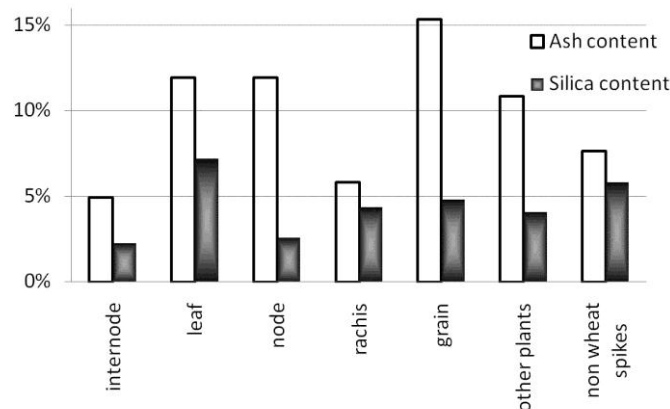


Fig. 2. Ash and silica content of bale components

Figure 3 indicates that the ash content of leaves and internodes was nearly equal at approximately 82% of total content. The node, with 13.73% ash content, is another important ash source of wheat straw. Although the leaves constituted 25.92% of straw bale mass, they contributed more than half of all of the silica in the bale (Fig. 4).

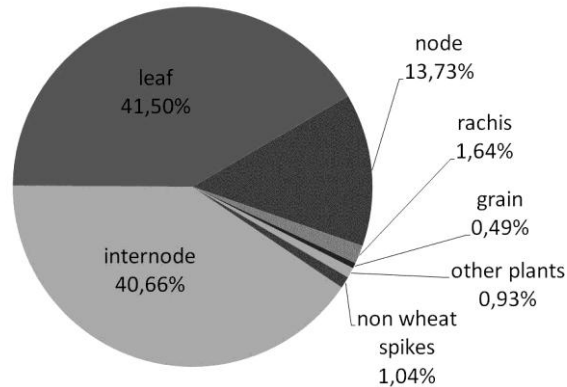


Fig. 3. Mass balance of ash

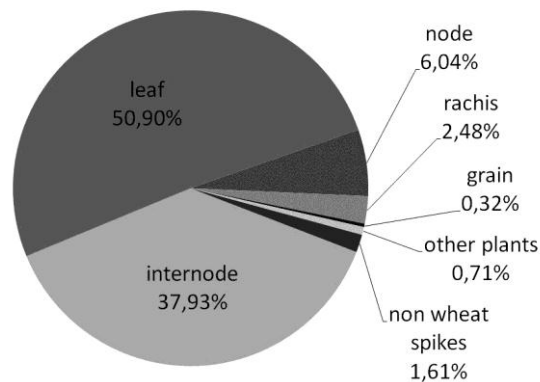


Fig. 4. Mass balance of silica

Aman and Nordkvist (1983) reported that 57% of the silica is in leaves, which is closer to the results obtained in this study. Meanwhile, their results for silica content in the node and internode were nearly equal, but in this study it was found that the silica content in the internode was six times more than that from the node.

For the internode silica, it was observed that phytoliths are mainly sinuous-shaped epidermal long cell phytoliths (Fig. 5). The leaf silica includes epidermal long cells, stomata phytoliths, and some amorphous silica bodies (Fig. 6). In the node, no large phytoliths were observed, and silica was only present in small amorphous particles (Fig. 7).

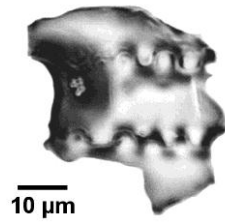


Fig. 5. Epidermal long cell phytolith from internode

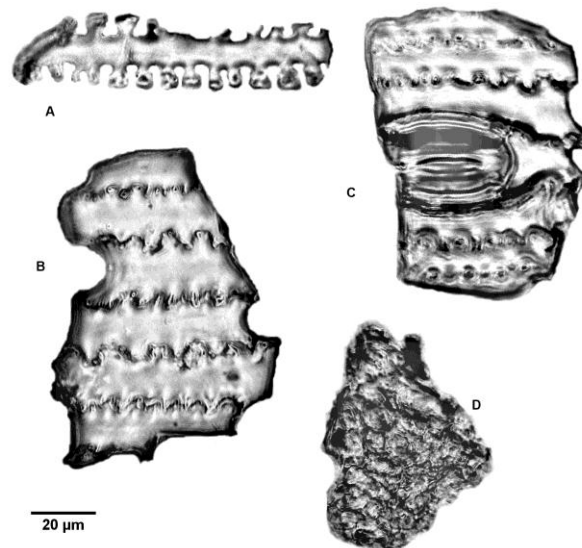


Fig. 6. Phytoliths from internodes: A) epidermal long cell phytoliths, B) epidermal long cell phytoliths, C) stomata phytoliths, and D) amorphous silica

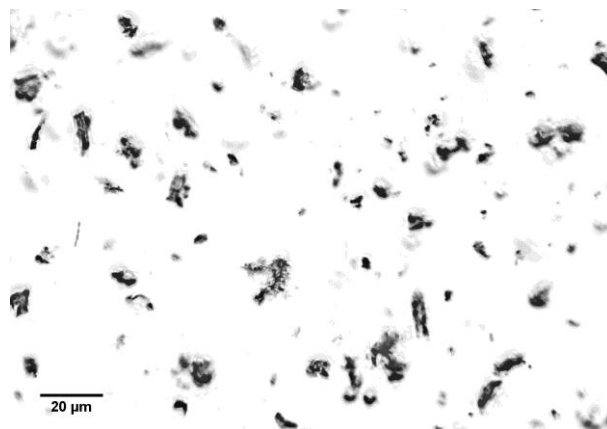


Fig. 7. Silica from node

The phytoliths in wheat, rachis, and other plants were not thoroughly destroyed during sonication (Figs. 8 through 10). Therefore, their abrasive effect will be higher than that represented by the mass balance measurement.

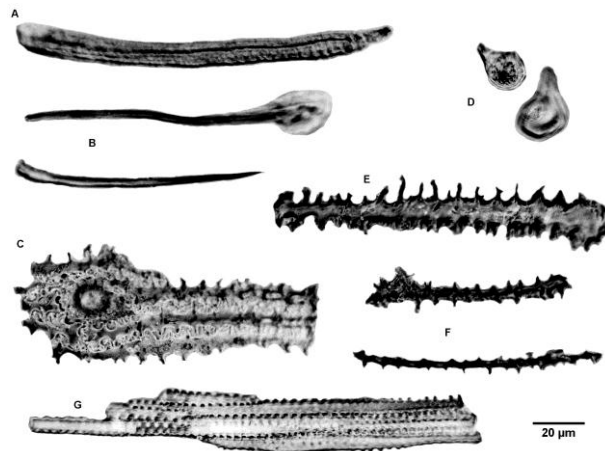


Fig. 8. Phytoliths from rachises: A) hair cell, B) hair cell, C) trichome base phytolith, D) trichome (prickle phytolith) hair cell, E) dendriform phytolith, F) rod-shaped phytolith, and G) dendriform phytolith

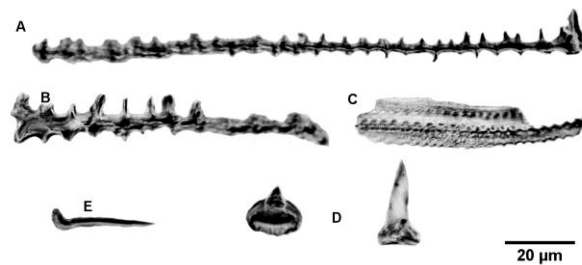


Fig. 9. Phytoliths from non-wheat spikes: A) rod-shaped phytolith, B) rod-shaped phytolith, C) dendriform phytolith, D) trichome (prickle phytolith) hair cell, and E) hair cell

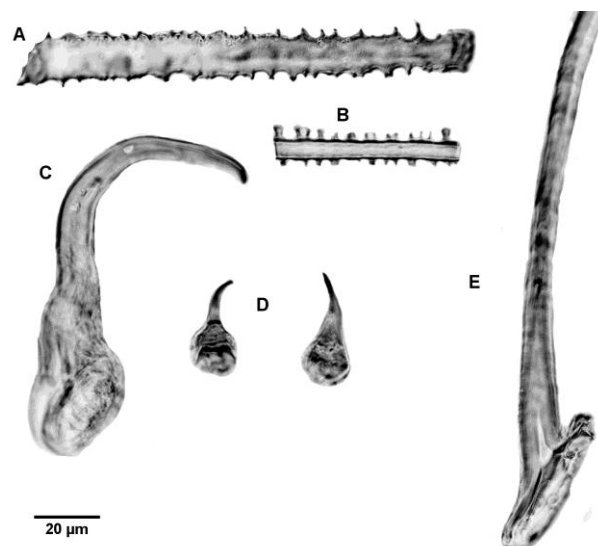


Fig. 10. Phytoliths from other plants: A) dendriform phytolith, B) dendriform phytolith, C) hook, D) trichome (prickle phytolith) hair cell, and E) hair cell

Pan *et al.* (1999) investigated the ash and silica content in rice straw, and small differences were observed between silica ratios in raw material and the resulting pulp. About 75% of the silica in rice straw was retained after pulping. This and our findings indicate that only the results from samples with equal leaf content will be comparable.

Destroying the long silica bodies inside of the fiber will increase the flexibility of the fibers, and the flexible fibers will contribute to an increase of the strength properties of straw pulp, as reported by Csoka *et al.* (2008).

Removing the part of straw with high silica content from pulping material will reduce problems with black liquor recovery and pulp quality. Hess *et al.* (2003) reported good results for mechanical separation of wheat straw stems with plot harvesting equipment. In-field physical separation was suggested, leaving the remaining components in the field to build organic matter and contribute to soil nutrients. However, fire risk and strong wind must be considered in arid landscapes. The straw can be separated out-of-field into internode and fine fractions. While the internode fraction goes to pulping, the fines go to other applications requiring high silica content. For example, the pozzolanic properties of wheat straw ash (Biricik *et al.* 1999) can be utilized.

CONCLUSIONS

1. Despite a small loss of leaves during mechanical harvesting, they still contribute most substantially to the wheat straw's silica content. The wheat leaf contains both sheath and blade. During mechanical harvesting, the blade content is preferentially reduced because the sheath is wrapped around the internode.
2. Further leaf removal (lighter blades and sheaths) during preparation of straw for pulping will reduce the silica content by 2% for every 1% of leaf content. Reduction of rachis and non-wheat plants will also decrease the abrasiveness of straw pulp.

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