Preparation of Biosilica-enriched Filler and an Example of its Use in a Nano-Particle Retention System

Jan Pekarovic, Alexandra Pekarovicova and Paul D. Fleming III.

Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University, A-231 Parkview, Kalamazoo MI 49008

ABSTRACT

Silica deposited within the plant tissue in small bodies –phytoliths is leached by an alkaline solution. Up to 70-75% of biosilica from wheat/rice straw becomes solubilized. The reaction kinetics is shown. Solubilized biosilica is recovered and reused in the papermaking process, via the causticizing reaction. The chemical composition, surface charge, charge demand and size distribution of newly designed filler is shown. The positive effect of this filler in nano-particle retention system is demonstrated.

INTRODUCTION

Most of the non-wood fibers for papermaking are derived from annual plants. The advantage of annual plants is that they can be grown on farmland and harvested each year with high yields (5-20 ton/ha depending on the crop type). As renewable resources, they can be replaced annually, compared with the much longer growth cycle for wood.

Non-wood pulp production, which represents less than 10% of the total world's pulp source, is based primarily on straw (46%), bagasse (14%), and bamboo (6%). Agricultural by-products account for 73% of the world's non-wood capacity, while natural plants such as reed and bamboo account for 18%, and the remainder consists mainly of industrial crops *(1).*

In North America, there are over 200 million tons of agricultural residue, (wheat, rice, corn, flax, barley and other cereal grain straw) that are produced every year after harvesting. Although some of these residues must be left in the field for soil conservation purposes, the bulk of the residues are available for industrial use. The U.S. and Canada have an abundance of agricultural residues, which could be used for pulp and paper production. Wheat straw and corn stalks represent the most underutilized fiber resources in the U.S. *(2).*

Like wood, straws are primarily composed of cellulose, lignin and hemicelluloses. But straws also contain significant amounts of pectins, proteins and, most importantly, inorganic compounds (ash), most weight percent of which is silica *(3, 4.)* The ash component of plants varies greatly between families of plants as well as between individual species. The largest mineral component of ash, in perennial grasses, is silica. The main difference in silica contents between perennial grass species is often related to the photosynthetic mechanism of the grass, and to the amount of water being transpired by the plant *(5)*. Within species, the water use efficiency will fluctuate depending on the region in which the crops are grown, and on the soil type *(6, 7)*.

The total holocellulose content of wheat straw is similar to that in trees. In comparison with wood, straw contains less cellulose. Xylans are the principal hemicelluloses of hardwoods and straws, analytically determined as pentosans. The lignin content of wheat straw (16 - 21 %) is significantly lower than that of softwoods (26 - 34 %), and hardwoods (23 - 30 %). Cereal straws have relatively high silica and potassium content. Wheat straw contains 4-10% silica as small crystals embedded in the straw, rice straw has an even higher silica content of 9-14%, and other cereals such as barley, oat and rye straw have 1-6% silica. Wood, on the other hand, has silica content of less than 1%.

Silica is distributed throughout the straw stem and is most concentrated in small bodies called phytoliths ("silica bodies", "silicophytoliths"), which cover the outer surface of the stem *(8).* Studied phytoliths generally range from a few to several tens of micrometers. Silica deposits in terrestrial plants occur most commonly in the form of particles of characteristic shape (dumbbells, saddles, bowls, boats), that are generally not diagnostic to the genus or species taxonomic level. Research efforts focused on biosilicification made by marine living sponges and unicellular algae have led to the finding of unique remarkably complex structures. Recent studies of silica structures made by living sponges show that this remarkable annular substructure of demosponge biosilica spicules deposits material that is nano-particulate, with a mean particle diameter of 74 ±13 nm *(9)*.

The biological reason for this is unknown, but it has been established that silicon is an essential element for plant growth. Recent research recognizes importance of silica in plant growth, disease, stress, pest resistance etc. Silica plays very important role not only in rice, wheat and sugarcane which are silica loving crops but crops like vegetable crop, fruit crops and other field crops.

It was reported that silicon in living plants is present in three basic forms: 1) insoluble silica (90%), 2) silicate ions (0.5-8%) and 3) colloidal silicic acid (0-3.3%) *(6)*. The insoluble silica in plant tissue (epidermal cell wall) is generally a clear, colorless and isotropic deposit with an index of refraction of 1.42 to 1.44. This amorphous silica deposit found in the dumbbell-shaped cell is frequently referred as biological opals.

The ash, and most specifically, the silica, remains the greatest impediment to the establishment of commercial straw pulping. Silica is extremely alkali soluble and its presence in spent liquors inhibits conventional chemical recovery process in three ways: 1/ by scaling multiple effect evaporators, 2/ by forming a colloid in the smelt tank reducing causticizing efficiency, and 3/ by forming glass in the lime kiln on lime particles. Therefore, as much silica must be removed from the recovery cycle as gets into the process with the raw material.

There have been many attempts made to resolve the silica issue, including black liquor desilication with carbon dioxide (flue gases), two-stage causticizing desilication method, green liquor desilication with lime, the incorporation of a sixth evaporator, used when an evaporator is being cleaned, and the use of ammonium- or potassium-based pulping with the liquor disposed of as a fertilizer *(3, 10).* Also, incorporation of some of the pulping liquor into the product can partially avoid silica-related chemical recovery problems *(3).* The appropriate pretreatment (dry cleaning) of straw is one of the solutions to minimize scaling problems in the recovery system. The dry cleaning system is fairly simple; it has low specific power consumption and its investment costs are rather low. Reductions in the silicon content of 20 to 50 % in straw have been reported *(10, 11).*

We already proved the beneficial effect of sodium carbonate as a silica-leaching agent *(12)*. Under the conditions of the experimental design, a desilication rate of 50-75 % can be reached. Sodium carbonate, with its additional hemicelluloses conservation effect, might be an interesting impregnation agent.

Precipitated calcium carbonate (PCC) is one of the most common fillers used in papermaking, paper coating, and polymer composites. Filler structure modification using novel polymer coating technique and new filler synthesis represent the methods of making a composite filler/pigment with an excellent combination of optical, surface and mechanical properties *(13-17)*.

Retention of the individual components presented within the papermaking furnish (lignocellulosic fibers, fines, inorganic/organic fillers, natural/synthetic polymers, and other additives) is critical to the properties and quality of the paper sheet as well as minimizing pollution and cost. Interaction between furnish components are controlled by electrokinetics, how the various charges of the system interact with each other. Because most of the individual components of the paper furnish have a net anionic charge (fibers, fines, fillers), they tend to be dispersed and therefore tend to pass through the wire unless mechanically retained by the filtrating action of the web. PCC particles carry a surface charge when dispersed in water. This naturally electrostatic positive charge, expressed by zeta potential, can be affected by other substances adsorbed on the surface to drive it negative.

To improve retention of the individual components of the furnish onto the surface of the fibers, thus improving the dewatering and consequently paper machine running at higher speeds, three general retention systems were developed. Compared to the single and dual polymer retention systems, nano-particle-based retention systems improve both – retention and dewatering. Besides this, sheet formation and dry strength might be improved. These dual retention system use cationic product with the coagulation/flocculation abilities (cationic starch and/or cationic PAM), and small micro/nano-particles negatively charged (aggregated, colloidal silica nano-particles), that can attach itself to the stock cationic sites. The size of primary silica particles of the newly designed retention systems is about 3-4 nm, with a very high specific surface area of about 800 m^2/g.

The aim of this study is to evaluate the integral use of rice straw for the papermaking process, including the silica wet extraction/leaching, and causticizing of the silica-enriched spent liquor with the aim to prepare and reuse the silica-enriched filler ($CaCO_3$) in the following paper making process. The concept of agricultural residues (straws) processing is submitted, including solubilization of nano/micro particles of silica deposits, and retention of silica-enriched calcium carbonate filler in papermaking furnish via nano-particle retention system.

EXPERIMENTAL

Raw material: Rice straw *(Oryza sativa)* from the 2003 California harvest was cut into 15 to 20 mm long strips and hand cleaned of sand and dust prior to experimentation. The straw, yellowish in color, was of high quality. It was stored at a solids-content of about 94 %. Whole stems including the leaves and rachis, were used.

Procedures and methods: in addition to the analytical methods listed in **Table 1**, further methods used in the study were as follows:

- *Suspended Solids* in– T-692
- *Total Solids* **–** T-625
- *Silica content in liquors (HACH Heteropoly Blue Method No. 8186)*
- *Sodium carbonate and residual alkali (Differential Method)*
- *Analysis of lime* –T-6178*
- *Zeta potential of filler's particles*

* Average "Available lime index" of the lime prepared in the laboratory conditions was 98.1% CaO.

Rice straw impregnation: Impregnation of a rice straw sample was conducted in a 6.5 L stationary batch digester (M&K Systems Inc.) equipped with a electrical heat exchanger and a liquor circulation system. The experiment was maintained at the conditions as follows:

160 grams of air dried rice straw, with 6% of moisture content, were soaked with 3,000 mL of cold tap water (ratio of RS to liquid equals to 1:20) at the ambient temperature. After the digester was heated up to the temperature of 95-96 ^{o}C, 38.5 grams of anhydrous Na_2CO_3 (15% of Na_2O on oven dried {o. d.} material) were dissolved in small amount of water and added into the digester. The time of the impregnation at the controlled temperature and atmospheric pressure was 30 minutes.

At the end of the experiment, the pulp was washed copiously with fresh hot tap water to a neutral pH. For chemical analysis, the wheat straw and pulp was ground in a Wiley mill and the fraction smaller than 40 mesh was collected. After the impregnated rice straw was washed and air-dried, total yield, total ash, and acid insoluble ash were determined. In the sample of black impregnation liquor (BIL) (collected approx. 2.2 L) determination of concentration of residual sodium carbonate, total suspended solids, total solids, total ash, acid insoluble ash, and concentration of solubilized silica in filtered sample was performed.

Causticizing of impregnation black liquor: 1200 mL of non-filtered BIL were causticized with 12.75 g of CaO (Na_2CO_3 to CaO molar ratio equal to1:3) in a 2L glass beaker, provided with the magnetic stirrer, at the temperature of 95 ^{o}C for 30 minutes. After the causticizing reaction the sediment was allowed to settle down in the sedimentation cylinder. 1200 mL of causticized black impregnation liquor (CBIL) was separated and stored. Sediment was divided to two separate fractions – course and fine. Both of the fractions were stored in 500 mL of DI water in plastic bottles. Concentration of residual sodium carbonate, and residual solubilized silica in CBIL was determined. The quantities of both of sediment fractions, total and acid-insoluble ash content in them were also determined.

Retention of biosilica-enriched filler in nano-particle-based system: because the straw pulp is expected to be used first of all in corrugated medium production, commercial fluting (ARVCO Container Co.) was chosen as the prime source of the fibers. Samples of fluting were disintegrated with tap water in the TAPPI disintegrator for 10 minutes, and the degree of freeness was determined (575 mL CSF). For the retention study square handsheets were prepared using a Noble & Wood sheet machine, with the approximate basis weight of 145-150 g/m^2.

After the disintegration, sample of commercial polyacrylamide (high molecular weight solid polymer) was added first into the slurry (0.25% consistency) under the continuous stirring at the amount of 0.5% based on the o.d. pulp. After the mixing time of 10 minutes, different types of fillers (commercial PPC, silica-enriched calcium carbonate – BLPCC) were added into the separate portion of the slurry at the level of 6% based on o.d. pulp. Two portions of BLPCC (fine and coarse) were mixed together prior the adding in the original proportion of them. After additional stirring (10 minutes), the sample of colloidal silica was added at the charge of 0.2 % based on the o.d. pulp. Subsequently the standard handsheets were prepared, and the ash content, as the parameter of filler retention, was determined.

The solutions of different chemical samples used in this part of study were freshly prepared separately by dilution in DI water as per the procedures provided by the suppliers.

RESULTS AND DISCUSSION

Chemical analysis

As the first step, before carrying out the impregnation/desilication experiments, a chemical analysis of the rice was performed in accordance with TAPPI Test Methods. The results of analysis are listed in **Table 1**. The table also contains already published results of wheat straw chemical analyses *(13).* Different types of the ash in both of the raw materials were the main objects of interest. The total ash content in non-processed rice straw was 9.7%, and the acid insoluble ash was 5.0%. These not surprising much higher numbers (compare with the wheat straw) represent the average levels of the ash content in rice straw, while in some samples the content of total ash and acid insoluble ash can vary depend on the plant species and the type of the soil *(6)*. Because acid insoluble ash, determined by any of the methods available, could contain mainly silica or silicates undissolved under acidic conditions, we use the term “desilication” instead of “deashing”.

Impregnation/Desilication

The temperature, time, and chemical charge were assumed to be the important properties influencing the process of impregnation/desilication. The significance of these three was analyzed with the central composite rotatable design method *(18).* The first step was to define the range of every single variable. With the computer software, a set of 20 experiments was generated. Second-order polynomial analysis of the experimental data led to different quadratic (second-order) equations. Although showing of the detailed experimental results was not the goal of this presentation, the strongest impact of temperature and time on the impregnation step was confirmed.

The statistical program allows displaying the effect of the single variables in 2-D or 3-D contour forms. The desilication kinetics of wheat and rice straw is shown in **Figure 1**. Because the time of the impregnation was found as the parameter with the strongest influence on every single dependent variable (and the sodium carbonate with the lowest influence), the 2-D contours at constant charge of sodium carbonate (10% Na_2O on raw material) are displayed.

In both of these figures, the curves have a very similar shape, from which the significant influence of temperature can be easily recognized. As seen in this contour, at the conditions of the central point of the experimental design, the desilication rate: 50% for wheat straw, and 27% for rice straw can be reached. At the higher temperatures, the desilication rate can reach 70 - 75%, and approximately 40%, respectively.

The most important fact is that even low levels of sodium carbonate charge cause leaching of silica (acid insoluble ash) from the raw material. The charge of sodium carbonate at the central points, even less, is sufficient to leach the significant quantity of ash/silica, in the first period of the impregnation phase of the process. It seems that part of the silica placed on the surface of the stem is easily affected and removed. Prolonged processing could have a beneficial effect on deashing, but, on the other hand, could negatively influence other important process parameters, i.e., the yield.

There are no critical requirements with respect to the time, temperature and pressure for performing the above-described impregnation step. All three of these variables depend on the quality and type of raw material, the extent of desired desilication, the desired quality of the silica-containing impregnation black liquor, the economics of the impregnating step, and subsequent causticizing of the silica-containing impregnation black liquor.

Unfortunately, during the impregnation of wheat straw, a part of the organic compounds is also removed, while absolute selective leaching of silica is a problem not yet solved. Removal of the organic part of wheat/rice straw leads to decreasing of total yield values. In the context of time and temperature, the effect of sodium carbonate has less importance.

There are some reasons why sodium carbonate was chosen as the impregnation chemical. The first reason comes from industrial experience with sodium carbonate application in high yield pulping of fluting production. The process is well known as “non-sulfur pulping”, and is particularly suitable for either sole wheat straw pulping or wood/wheat straw mixed pulping. The second reason comes from the fact that NaOH is considered to be an effective extracting chemical for sugars and hemicelluloses, part of the lignocellulosic materials. That is why Na_2CO_3 with its hemicelluloses conservation effect may be a more interesting impregnation/desilication agent.

A general diagram of the laboratory experiment, desilication and causticizing step included, is shown in the **Figure 2.**

Causticizing of black impregnation liquor (BIL)

For the causticizing of black rice straw impregnating liquor purposes, and preparation of a sufficient quantity of silica-enriched precipitate, cca 2.2 L of this liquid media was prepared. The conditions of rice straw desilication were chosen as stated in experimental part of this presentation.

The result of the chemical analysis of rice straw as the raw material, as well as the impregnated/desilicated rice straw, are shown in **Table 2.** From the results, it is obvious that almost 40% of the acid insoluble was removed and passed into the black impregnation liquor. This number is in good accordance with the experimental results of rice straw desilication (**Figure 1).** Supporting results of black impregnation liquor are shown also in the **Table 3.** From the results, is evident, that from the original amount of sodium carbonate (12.8 g/L), almost 50% of it was consumed to solubilize ash/silica, respectively part of organic constituents present within the raw material.

Because the presence of other substances (except the solubilized silica) in black impregnation liquor, which can effect the causticizing reaction, an excess of lime was added (Na_2CO_3 to CaO molar ratio equal to 1:3). Lowering of all analytical data shown in **Table 3** refers to the efficient progress of the causticizing reaction, especially from the silica removal point of view. The causticized solution contains mainly precipitated calcium carbonate, sodium hydroxide, excess lime that doesn’t react with sodium carbonate and other components, such as soluble lignin, hemicelluloses and soluble silica, which enter the causticizing reaction and which may or may not be entrapped with the precipitated calcium carbonate.

After the causticizing step, precipitated silica-enriched calcium carbonate can be separated from the causticized impregnation liquor by any suitable type of separation process, where sedimentation and filtration techniques are being preferred. Although there is no critical time, temperature and pressure conditions required for separation of the precipitated silica-enriched calcium carbonate from the causticized impregnation liquor, it is generally known that higher temperatures have a positive effect on the settling velocity in a sedimentation process and higher pressures have a positive effect on separation in filtration processes. The separated causticized black impregnation liquor is considered to be silica-free and can be used as a washing liquor, dilution media or make-up media in different steps in the process.

In the laboratory conditions, precipitated silica-enriched calcium carbonate was allowed to settle down in the sedimentation cylinder overnight. Two separate layers of the sediment were evident in the tapered bottom of the cylinder. The main difference was based on their color (coarse darker than fine), and presumably on their average particle size. The results listed in the **Table 4** illustrate the main difference in their quantity (predominantly fine portion), while the difference of total ash and acid insoluble ash content can be assumed to be not significant. Interesting is the content of the organic portion present within the sediments, that achieves the values of 20-30%. The presence of these accessory matters is expected to significantly influence the surface and overall properties of the sediment particles.

Silica-enriched filler in nano-particle retention system

For this part of the study, a relatively simple aqueous system was chosen, consisting of recycled fibers derived from fluting used for corrugated media production, two types of filler (commercial PPC and biosilica-enriched calcium carbonate), and components of nano-particle retention systems (cationic polyacrylamide and nano-scale colloidal silica), added into the system successively. While the cationic polymer forming bridges between negatively charged particles is added first, the anionic colloidal silica nano-particles are added very late, in the papermaking technology just before the head box.

Before the experiment was done, in addition to the chemical analysis of BLPCC, the surface charge (Zeta potential) of the fillers was determined. The results obtained are listed in **Table 5**. Not surprisingly, commercial type of precipitated calcium carbonate shows positive zeta potential, dependent on alkalinity of aqueous system. Unlike this, biosilica-enriched calcium carbonate prepared via causticizing of black impregnating liquor carries negative surface charge, slightly influenced by the pH. This finding can be accomplished by the presence of organic materials, entrapped within the calcium carbonate particles. Based on the difference of surface charge character, different behavior of these types of fillers in retention system was expected.

Results of the retention experiment are shown in **Figure 3.** Extent of the filler retention is expressed as the total ash content presented in the handsheets. Due to the ash content of virgin recycled pulp (1.8 % - baseline), and the charge of filler -6% on o.d. fibers, the retention of commercial PPC reached the value of 37%, and the retention of biosilica-enriched filler 53%. Although these numbers have to be statistically confirmed, common and usual behavior of these fillers in the commercial retention systems is expected.

Although the application of these types of filler and their influence on mechanical properties of different paper products is not the main objective of this presentation, preliminary laboratory results were obtained. They demonstrate, that the presence of biosilica-enriched filler prepared under laboratory conditions has a not to be unambiguously detrimental element in the furnish of paper board (fluting). On the contrary, some of chosen parameters have shown the improvement. Particularly the properties important for the corrugated medium substrate (fluting) – CMT, Gurley stiffness, and Ring crush test. Of course, these statements are valid for the certain pulp furnish and the content of total ash in the handsheets – up to 5%.

CONCLUSIONS

This study analysizes the concept of processing of agricultural residues (straws), which includes dissolution of nano/micro particles of silica deposits, following by retention of silica-enriched calcium carbonate filler in papermaking furnish via a nano-particle retention system. Rice straw *(Oryza sativa)* with 9.7% of total ash content; and 5.0% of acid insoluble was processed. Experimental design was used to optimize the cooking conditions. In the impregnation step at the conditions of the central point of the experimental design, the desilication rate 50% for wheat straw and 27% for rice straw can be reached. At the higher temperatures, the desilication rate can reach 70 - 75%, and cca 40%, respectively. From the analysis of the impregnation liquor and the content of residual sodium carbonate presented in black impregnation liquor, it is evident that almost 50% of it was consumed to solubilize ash/silica, along with part of organic constituents present within the raw material.

The causticizing reaction provided on black impregnation liquor appeared to be efficient, especially from the silica removal point of view. Almost all solubilized silica was entrapped with the precipitated calcium carbonate. Two different portions of the sediment (coarse and fine) were collected and analyzed. The difference of total ash and acid insoluble ash content in both of the fractions can be assumed to be not significant. Interesting is the content of organic portion present within the sediments, which achieves the values of 20-30%.

Silica-enriched calcium carbonate, with the negative surface charge (Zeta potential) was used as the filler in a nano-particle retention system. In the relatively simple aqueous system cationic polyacrylamide and colloidal nano-particle silica were chosen as the retention aids. The retention of commercial PPC reached the value of 37%, and the retention of biosilica-enriched filler 53%. Although these numbers have to be statistically confirmed, common and usual behavior of these fillers in the commercial retention systems is expected.

REFERENCES

1. Paavilainen, L.: European prospects for using non-wood fibers, *Pulp Paper Int.* **40**(6):61(1998).
2. Hurter, R., Riccio, F.: Why CEO's don't want to hear about non-woods - *or should they? TAPPI Proc. North American Non-wood Fiber Symposium,* Atlanta, GA, p.1 (1998).
3. Watson, P. A., Bicho, P. A. and Stumborg, M. A.: Wheat straw: a viable fiber source for Canada? *Pulp & Paper Canada* **99**(12):46(1998).
4. Epstein, E: "*Mineral metabolism*". In: Bonner J., Varner J.E. (eds.) Plant biochemistry. Academic Press, New York and London, p. 438-466 (1965).
5. Black, C.C.: Ecological implications of dividing plants into groups with distinct photosynthetic production capacities, *Advanced Ecological Resources* (7):87(1971).
6. Jones, L. H. P., Handreck, K. A.: Silica in soils, plants and animals, *Advances in Agronomy* (19):107(1967).
7. Sander, B.: Properties of Danish biofuels and the requirements for power production, *Biomass and Bioenergy* **12**(3):177(1997).
8. Parry, D. W., Hodson, M. J. and Sangster, A. G.: Some recent advances in studies of silicon in higher plants, *Phil. Trans. R. Soc. London.* (B304):537(1984).
9. Weaver, J. C., Pietrasanta, L. I., Hedin, N., Chmelka, B., Hansma, P.K., Morse D.E.: Nanostructural features of demosponge biosilica, Journal *of Structural Biology* (144):271(2003).
10. Paavilainen, L.: Modern non-wood pulp mill – process concepts and economic aspects, *TAPPI Proc. North American Nonwood Fiber Symposium*, Atlanta, GA, p.227 (1998).
11. Misra, D.K.: "Cereal straw", In TAPPI Press (ed.), Atlanta, Pulp and Paper Manufacture , Vol. 3, p.82 (1993).
12. Pekarovic J., Pekarovicova A., and Joyce T. W.: Desilication of agricultural residues – the first step prior to pulping, *Appita Journal* **58**(2):130-134(2005).
13. Deutsch D. R., et al.: Process for the preparation of discrete particles of calcium carbonate, *US Patent 6,294,143 (2001).*
14. Haverinen J. P., et al.: Composite precipitated calcium carbonate/silicon compound pigment and method of making same, *US Patent 6,623,555 (2003).*
15. Adams, Jr., et al.: Silica-coated alkaline earth metal carbonate pigment, *US Patent 6,136,085 (2000).*
16. Gill R.A.: Modified filler material for alkaline paper and method of use thereof in alkaline paper making, *US Patent 5,380,361 (1995).*
17. Wason S.K. et al.: Precipitated encapsulated paper pigments and methods, *US Patent 5,262,239 (1993).*
18. Hicks, C.R.: *"Response-surface experimentation"*, In Sunders College Publishing (ed.) Fundamental Concepts in the Design of Experiments, N.Y., p.402 (1993).