A method of cellulose raw material desilication involves the steps of impregnating the cellulose raw material with a solution containing sodium carbonate to form a silica-containing impregnation black liquor and an at least partially desilicated raw material, separating the silica-containing impregnation black liquor from the at least partially desilicated raw material, causticizing the separated silica-containing impregnation black liquor to precipitate silica-enriched calcium carbonate and separating the precipitated silica-enriched calcium carbonate from the causticized impregnation liquor. Up to 100% of the silica contained in the cellulose raw material can be removed before the raw material is processed by any of conventional pumping methods.
PROCESS FOR REMOVING SILICA FROM CELLULOSIC MATERIAL

FIELD OF THE INVENTION

[0001] The present invention relates to a method of removing silica from a cellulose raw material, such as bamboo, bagasse, reed and straw, prior to the cellulose raw material being converted into a pulp by a chemical or mechanical delignification processes.

BACKGROUND OF THE INVENTION

[0002] Non-wood cellulosic fibers are a percentage of the world’s pulp source, representing less than 10% of the total pulp production. Non-wood pulp production primarily utilizes straw, bagasse, bamboo and reed. Agricultural by-products make up 73% of the world’s non-wood pulp capacity while natural plants such as reed and bamboo account for 18% and the remainder consists mainly of industrial crops.

[0003] Current trends indicate that the global consumption of paper making fibers would increase to approximately 425,000,000 tons by the year 2010. At the present time, it is not known where the estimated millions of tons of fiber needed by the year 2010 will come from. An abundance of agricultural residues are produced in the United States and Canada, which could be used for pulp and paper production with wheat straw and corn stalks representing the most undemilized fiber resources in the United States.

[0004] The macro-chemical composition of non-wood cellulosic raw materials such as wheat straw does not deviate materially from that of hardwood. The total holocellulose content of wheat straw is very similar to that of trees. In contrast with wood, straw contains less cellulose. The lignin content of wheat straw is typically from 16% to 21% and significantly lower than that of softwoods, which is typically 26% to 34%, and hardwoods, which is typically from 23% to 30%. Cereal straws have relatively high silica and potassium content. The ash content of straw is invariably much higher than that of most other fibrous materials while Xylans are the principal hemicellulose contained in hardwoods and straws, analytically determined as pentosans.

[0005] The greatest impediment to the use of non-wood cellulosic raw materials in commercial pulping is the ash, and more specifically silica, contained therein. Silica is distributed throughout the straw stem and is concentrated mostly in small bodies called phytoliths, which cover the outer surface of the stem. Silicon is typically present in living plants in three basic forms: insoluble silica in an amount of 90%, silicate ions in an amount of from 0.5% to 8%, and colloidal silicic acid in the amount of 0 to 3.3%. The insoluble silica in plant tissue is generally a clear, colorless and isotropic deposit with an index of refraction of 1.42 to 1.44. This amorphous silica deposit is found in a dumbbell-shaped cell referred to as biological opals.

[0006] There have been many efforts to accomplish the removal of silica from non-wood cellulosic materials in a simple and economical fashion, including black liquor desilication with carbon dioxide from flue gases, two-stage causticizing desilication, green liquor desilication with lime, evaporation and the use of ammonium- or potassium-based pulping with the by-product liquor being utilized as a fertilizer.

[0007] U.S. Pat. No. 4,331,507 to Roberts discloses an alkaline-type pulping process for the manufacture of pulp from silica-contaminated raw materials where a quantity of aluminum oxide sufficient to react with silica and sodium hydroxide present in the process is introduced into the pulp liquor to precipitate silica as a soda lime.

[0008] U.S. Pat. No. 4,504,356 to Mülter et al discloses a continuous process for removing silica from spent pulping liquors, which have been obtained by the alkaline digestion of annual plants by pre-concentrating the spent liquor and contacting it with a carbon dioxide-containing gas. Silica precipitates, is removed from the treated liquor and then washed with water and causticized by the addition of lime or milk of lime. The solid and liquid phases are separated from each other and the resulting residue is combusted.

[0009] U.S. Pat. No. 4,941,945 to Pettersson discloses a method of cleaning green liquor of solid particulate impurities by removing solid particles out of unclarified green liquor prior to the subsequent complete causticizing of clarified green liquor by adding caustic lime to the clarified liquor. The caustic lime is added to the unclarified green liquor during agitation prior to the removal of the solid particles in an amount of 0.5% to 10% of the caustic lime needed for the subsequent complete causticization. Waste liquor obtained during the digestion of wood is evaporated to give concentrated waste liquor, which is then burnt in a soda recovery boiler. A slaked that obtained is then in smelt spouts down into a tank where it is dissolved in green liquor obtained by the washing of lime sludge in the causticizing department to produce green liquor. The green liquor is sent to a green liquor clarifier for removing solid particles therefrom by sedimentation.

[0010] U.S. Pat. No. 6,074,521 to Engdahl et al discloses that it is known to remove silicon from green liquor by adding lime to the green liquor whereby silicon precipitates with the lime, which may then be removed.

[0011] Chinese Publication No. 1103450 to Wang et al discloses a process for the removal of silicon from straw pulping black liquor which requires the addition of aluminum oxide and/or aluminum dihydrate from a by-product of an aluminum industry, and optionally a residue from a sodium chloride derived industry, or lime, to a straw pulping black liquor and separating the silica therefrom.

[0012] However, none of the prior art references discussed above disclose a simple and economical method of desilicating a cellulose raw material that is to be used in the pulp manufacture.

SUMMARY OF THE INVENTION

[0013] It is an object of the present invention to provide a method for removing silica from a cellulose raw material, which can be performed in a simple and economical manner.

[0014] It is a further object of the present invention to provide a method for removing silica from a non-wood cellulose material in a simple and economical manner.

[0015] It is still a further object of the present invention to provide a method for removing silica from a non-wood cellulose raw material selected from straw, bagasse, bamboo, reed and cornstalks in a simple and economical manner.
to produce a processed non-wood cellulose material which can be used subsequently in pulp manufacture.

**[0016]** DETAILED DESCRIPTION OF THE INVENTION

**[0017]** The present invention is concerned with the removal of silica from a cellulose raw material, particularly, a non-wood cellulosic material which can be straw, bagasse, reed, bamboo, cornstalks, and combinations thereof. Initially, the cellulosic raw material should be cut into long pieces of approximately 10 to 30 millimeters in length and then screened. This significantly reduces the content of silica in the raw materials up to 50%. After washing, the raw materials are then moisturized and preheated by steam or hot water to help improve the kinetics of the impregnation of the cellulosic raw material with a silica leaching agent to thereby improve the efficiency of silica removal.

**[0018]** The pretreated cellulosic raw material is impregnated with a solution comprising sodium carbonate to form silica-containing impregnation black liquor and in at least partially desilicated raw material. The sodium carbonate is preferably dissolved in an aqueous medium and, optionally, sodium hydroxide can be contained therein. The concentration of sodium carbonate in the impregnating solution is from 2.5 to 100 grams of Na₂O equivalents per liter of impregnating solution. If desired, an impregnating solution containing a higher concentration of sodium carbonate may be dissolved with any kind of technological water or waste aqueous media containing residual sodium carbonate to achieve the targeted amount of sodium carbonate or sodium carbonate and sodium hydroxide mixture to obtain the desired ratio of impregnating solution to raw material. The amount of sodium carbonate contained in the impregnating solution varies depending on the quality of the cellulosic raw material and the desired levels of desilication. The charge of sodium carbonate may be up to 25% based on oven dried weight of raw material and preferably is over 5%, most preferably 10%, Na₂O equivalent.

**[0019]** The ratio of impregnation liquid to cellulosic raw material can vary significantly depending on the quality of the raw material and normally is maintained in the range of from 1:2.5 up to 1:20. The ratio is maintained as small as possible while maintaining good impregnation operation, including good impregnating solution circulation to achieve even silica removal from the raw cellulosic material.

**[0020]** 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 causticization of the silica-containing impregnation black liquor.

**[0021]** Although the time, temperature and pressure for the impregnating step will depend on the variables discussed above, the time of the impregnation may take up to two hours, preferably up to one hour and most preferably 30 minutes. The temperature of the impregnation can range from at least 40° centigrade up to 180° centigrade with 100° centigrade being preferable and 70° centigrade being most preferable. The impregnation pressure may vary up to 880 kPa of saturated steam but most preferably impregnation is performed at atmospheric pressure.

**[0022]** The impregnating step at least partially desilicates the cellulosic raw material and will preferably completely desilicates the cellulosic raw material and forms silica-containing impregnation black liquor. The silica-containing impregnation black liquor is separated from the at least partially desilicated cellulosic raw material by any known suitable separation technique and is preferably separated by a screw press.

**[0023]** As with the impregnating step, there are no critical requirements with respect to time, temperature and pressure necessary for performing the separation of the silica-containing impregnation black liquor from the at least partially desilicated raw material. The time of separation will be dependent upon the retention time needed in the separation device and a preferable temperature is the temperature of the silica-containing impregnation black liquor entering the separation device. A preferred pressure of the separation step is atmospheric pressure but any other temperature and time parameters can be varied by one skilled in the art based on the conditions of the materials to be separated, the desired product quality and the separation device utilized.

**[0024]** After being separated from the at least partially desilicated cellulosic raw material, the separated silica-containing impregnation black liquor is causticized to precipitate silica-enriched calcium carbonate. Calcium oxide and/or calcium hydroxide is used to causticize the separated silica-containing impregnation black liquor and should be added in an amount at least equal to a 1:1 molar ratio of lime to residual sodium carbonate. The conversion efficiency of the causticizing step is dependent on the duration of the causticizing step, the temperature of the causticizing liquor and the quality of the calcium oxide-containing material.

**[0025]** In general, the causticizing reaction rate curves show two separate zones with an initial period having high values of reaction rate from the initiation of causticization up to 20 minutes at a temperature range of from 70° to 100° centigrade, at which a causticizing efficiency up to 50% is reached. The second time period is characterized by a very low reaction rate value and requires a much longer period of causticizing as equilibrium conversion is approached.

**[0026]** For economic reasons, changes in the incoming silica-containing impregnation black liquor are not expected so the time of causticizing will mostly be dependent on the quality and amount charged of calcium oxide. Moreover, an increase in the amount of calcium oxide charge may affect the causticizing step in two ways. It would increase the reaction rate of the causticizing reaction because most of the easily reacting part of the calcium oxide will be presented and it will also negatively affect the kinetics of the causticizing because of the higher particle concentration and higher concentration of residual, non-reactive slaked lime in the final solution which can cause problems with respect to the settling of lime mud, calcium carbonate, in the following step of separating silica-enriched sodium carbonate from the causticized impregnation black liquor.

**[0027]** The causticized solution may also contain 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.

**[0028]** After the causticization step, precipitated silica-enriched calcium carbonate can be separated from the caus-
ticized impregnation liquor by any suitable type of separation process, with sedimentation and filtration techniques being preferred. Although there is no critical time, temperature and pressure conditions required for separation of the precipitated silica-enriched calcium carbonate from the causticizing impregnation liquor, as is generally known, 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 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.

[0029] The present invention is further shown, but not limited by, the following examples.

[0030] Wheat straw (Triticum aestivum) from Michigan harvest area was chopped into 10 to 30 mm long strips and hand cleaned from sand and dust prior to the experiment. The straw, yellowish in color, was of high quality. The sample was stored at a dry content of about 94%. Whole stems, without leaves and rachis were used.

[0031] The impregnation of the wheat straw sample was conducted in a 6.5 L stationary batch digester (M&K Systems Inc.) equipped with an electrical heat exchanger and a liquor circulation system. The experiment was conducted at the conditions as follows: 160 grams of air-dried wheat straw with 6% of moisture content, 38.5 grams of anhydrous Na$_2$CO$_3$ (15% of Na$_2$O on o.d. material), liquor to wheat straw ratio—1:20, impregnation temperature—95°C, time of impregnation at the impregnation temperature—30 minutes.

[0032] Control sample: A sample of the wheat straw, containing 2.95% of total ash and 1.22% of silica (acid insoluble ash), was treated with the impregnating liquid (12.8 g Na$_2$CO$_3$/L) under the conditions mentioned above. After the impregnation step, the sample of impregnated wheat straw was washed and stored in wet conditions, and 2160 mL of impregnation black liquor were used for the following analysis and causticizing experiments.

[0033] The total yield from the wheat straw impregnation was 88.1%. The impregnated black liquor contained 23 mg of suspended solids per liter, total solids 19.3 g/L, total ash content (575°C) 13.6 g/L, silica content 0.582 g/L, and concentration of residual sodium carbonate 8.3 g Na$_2$CO$_3$/L. Based on the analysis provided, cca 35.2% of sodium carbonate in the impregnation liquor was consumed and 95.8% of silica was removed from the raw material.

[0034] Causticizing step: Causticizing of the impregnation black liquor obtained after impregnation of the wheat straw was performed in 50 mL PE ampoules at a temperature of 105°C and time of 6 hours. The sample of impregnation black liquor was filtered and not diluted. A different amount of quick lime prepared in the laboratory was added directly into the ampoules filled with the impregnation black liquor. After causticizing, the samples were clarified overnight by settling the sediment and then centrifuged at 2300 RPM for 5 minutes. A clear solution (Supernatant I) was separated, stored and used for silica content and residual sodium carbonate analysis. The amount of sediment was determined by drying at 105°C in an oven.

**EXAMPLE I**

[0035] In a step of causticizing impregnation black liquor containing predominantly residual sodium carbonate and dissolved silica, 25 mL of filtered impregnation black liquor was treated in a 50 mL PE ampoule under the conditions described above. 0.0778 g of powdered calcium oxide (quick lime) was added into the sample, which contained dissolved silica at a concentration of 0.582 g/L. The amount of quick lime added was 71.2% stoichiometrically equivalent to the amount of sodium carbonate present in the sample. After the causticizing reaction, an analysis of centrifuged and clarified spent liquor was provided. 42.4% of causticizing efficiency was determined, and the concentration of dissolved silica in the liquor dropped to a level of 0.542 g/L. Thus, the amount of dissolved silica was reduced by 9.3%.

**EXAMPLE II**

[0036] The following experiment was provided under the same conditions, except the calcium oxide (quick lime) was added at the amount of 123% stoichiometrically equivalent to the amount of sodium carbonate present in the sample. After the causticizing reaction, an analysis of centrifuged and clarified liquor was provided. 100% causticizing efficiency was determined and the concentration of dissolved silica in the liquor dropped to a level of 0.014 g/L. The treatment was effective in that the dissolved silica was reduced to 2.4% of the silica dissolved in the original impregnation black liquor. The concentration of residual dissolved silica (0.014 g/L) most probably comes from quick lime used for the causticizing steps, which contained 0.13% silica by weight. Taking this into consideration, the residual silica content may come from sources other than the raw material (wheat straw), so the desilicification efficiency in this example may be considered to be 100%.

**EXAMPLE III**

[0037] For the impregnation/desilicification of wheat straw, under the same conditions as mentioned above, the impregnating liquor with a Total Titratable Alkalinity of 10.0 g Na$_2$O/L was used with a ratio of Na$_2$CO$_3$:NaOH of 3:1 (in Na$_2$O equivalents). The impregnating black liquor contained residual sodium carbonate at a concentration of 5.5 g Na$_2$O/L and dissolved silica at a concentration of 0.595 g SiO$_2$/L. Into the sample containing dissolved silica at the concentration of 0.595 g/L, calcium oxide (quick lime) was added at the amount of 120% stoichiometrically equivalent to the amount of sodium carbonate present in the sample of impregnation black liquor (the same as in Example II). After the causticizing reaction, an analysis of centrifuged and clarified liquor was provided. 56.8% of causticizing efficiency was determined and the concentration of dissolved silica in the liquor dropped to a level of 0.249 g/L. The treatment had been effective in that the dissolved silica had been reduced to 41.8% of the silica dissolved in the original impregnation black liquor. Thus, 58.2% reduction of dissolved silica was achieved. Example III shows that the causticizing of the impregnation black liquor with sodium hydroxide contained therein is in principle possible, but with lower dissolved silica reduction efficiency, as well as a lowered causticizing efficiency.

[0038] The present invention allows for the separation of up to 100% of the silica originally contained in the cellulosis raw material and the complete separation of silica from the silica-contained impregnation black liquor in an economical and simple manner to provide a process cellulosis material that can be used at a paper pulping process.
What is claimed is:

1. A method of removing silica from a cellulosic raw material comprising the steps of:
   - impregnating the cellulosic raw material with a solution comprising sodium carbonate to form a silica-containing impregnation black liquor and an at least partially desilicated raw material;
   - separating the silica-containing impregnation black liquor from the at least partially desilicated raw material;
   - causticizing the separated silica-containing impregnation black liquor to precipitate silica-enriched calcium carbonate; and
   - separating the precipitated silica-enriched calcium carbonate from the causticized impregnation black liquor.

2. The method of claim 1, wherein the impregnating solution comprising sodium carbonate additionally comprises sodium hydroxide.

3. The method of claim 1, wherein the cellulosic raw material can be used in paper manufacture.

4. The method of claim 1, wherein the cellulosic raw material is an agricultural residue.

5. The method of claim 1, wherein the cellulosic raw material is a non-wood cellulosic material.

6. The method of claim 1, wherein the impregnating step takes place at a temperature of at least 40°C to approximately 100°C.

7. The method of claim 1, wherein the weight ratio of cellulosic raw material to impregnating solution comprising sodium carbonate is at least 2.5%.

8. The method of claim 1, wherein the impregnating step is carried out for at least 5 minutes.

9. The method of claim 1, wherein the sodium carbonate content in the impregnating solution is at least 5% of Na₂O equivalent.

10. The method of claim 1, wherein the separated silica-containing impregnation black liquor is causticized with calcium oxide or calcium hydroxide.

11. The method of claim 10, wherein the calcium oxide or calcium hydroxide is added in an amount at least equal to a 1:1 molar ratio of calcium oxide or calcium hydroxide: residual sodium carbonate in the separated silica-containing impregnation black liquor.

12. The method of claim 1, wherein the cellulosic raw material is selected from the group consisting of straw, bagasse, reed, bamboo, and cornstalks.

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