

FILLER-FIBER COMPOSITE

FIELD OF THE INVENTION

5 The present invention relates to a filler-fiber composite, a process for its production, the use of such in the manufacture of paper or paperboard products and to paper produced therefrom. More particularly the invention relates to a filler-fiber composite in which the morphology and particle size of the mineral filler are established prior to the development of the bond to the fiber. Even more particularly, the present invention relates to a PCC filler-fiber composite, wherein the desired optical
10 and physical properties of the paper produced therefrom are realized.

BACKGROUND OF THE INVENTION

 Loading particulate fillers such as calcium carbonate, talc and clay on fibers for the
15 subsequent manufacture of paper and paper products continues to be a challenge. A number of methods, having some degree of success, have been used to address this issue. To insure that fillers remain with or within the fiber web, retention aids have been used, direct precipitation onto the fibers have been used, a method to attach the filler directly to the surface of the fiber have been used, mixing the fiber and the filler have been used, precipitation within never dried pulp have been used,
20 a method for filling the cellulosic fiber have been used, high shear mixing have been used, fibrous material and calcium carbonate have been reacted with carbon dioxide in a closed pressurized container, fillers have been trapped by mechanical bonding, cationically charged polymers have

been used and pulp fiber lumen loaded with calcium carbonate have all been used to retain filler in fiber for subsequent use in paper. Most of the methods for fiber retention are both expensive and ineffective.

5 Therefore, what is needed is a filler fiber composite and a method for producing the same that is both effective in retaining the filler and inexpensive for the paper maker to utilize.

 Therefore, an object of the present invention is to produce a filler/fiber composite. Another object of the present invention is to provide a method for producing a filler/fiber composite. While
10 another object of the present invention is to produce a filler/fiber composite that maintains physical properties such as tensile strength, breaking length and internal bond strength. Still a further object of the present invention is to produce a filler/fiber composite that maintains optical properties such as ISO opacity and pigment scatter. While still a further object of the present invention is to provide a filler/fiber composite that is particularly useful in paper and paperboard products.

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RELATED ART

U.S. Pat. No. 6,156,118 teaches mixing a calcium carbonate filler with noil fibrils in a size of P50 or finer.

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U.S. Pat. No. 5,096,539 teaches in-situ precipitation of an inorganic filler with never dried pulp.

U.S. Pat. No. 5,223,090 teaches a method for loading cellulosic fiber using high shear mixing of crumb pulp during carbon dioxide reaction.

5 U.S. Pat. No. 5,665,205 teaches a method for combining a fiber pulp slurry and an alkaline salt slurry in the contact zone of a reactor and immediately contacting the slurry with carbon dioxide and mixing so as to precipitate filler onto secondary pulp fibers.

10 U.S. Pat. No. 5,679,220 teaches a continuous process for in-situ deposition of fillers in papermaking fibers in a flow stream in which shear is applied to the gaseous phase to complete the conversion of calcium hydroxide to calcium carbonate immediately.

U.S. Pat. No. 5,122,230 teaches process for modifying hydrophilic fibers with a substantially water insoluble inorganic substance in-situ precipitation.

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U.S. Pat. No. 5,733,461 teaches a method for recovery and use of fines present in a waste water stream produced in a paper manufacturing process.

20 U.S. Pat. No. 5,731,080 teaches in-situ precipitation wherein the majority of a calcium carbonate trap the microfibril by reliable and non-reliable mechanical bonding without binders or retention aids.

U.S. Pat. No. 5,928,470 teaches method of making metal oxide or metal hydroxide-modified cellulosic pulp.

U.S. Pat. No. 6,235,150 teaches a method of producing a pulp fiber lumen loaded with
5 calcium carbonate having a particle size of 0.4 microns to 1.5 microns.

The problem of insuring that filler materials, such as calcium carbonate, ground calcium carbonate, clay and talc, remain within fibers that are ultimately to be used in paper has been subjected to a number of proofs. However, none of the prior related art discloses a filler fiber
10 composite where the morphology of the filler is predetermined prior to introducing fibrils, a method for its production nor its use in paper or paper products.

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SUMMARY OF THE INVENTION

The present invention relates to a filler-fiber composite including feeding slake containing seed to a first stage reactor, reacting the slake containing seed in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry,
20 reacting the first partially converted calcium hydroxide calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide to produce a second partially converted calcium hydroxide calcium carbonate slurry and reacting the second partially converted calcium hydroxide calcium carbonate slurry in a third stage reactor in the presence of carbon dioxide and fibrils to produce a filler-fiber composite.

In another aspect, the present invention relates to a filler-fiber composite including feeding slake containing seed to a first stage reactor, reacting the slake containing seed in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry and reacting the first partially converted calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide and fibrils to produce a filler-fiber composite.

In a further aspect, the present invention relates to a filler-fiber composite including feeding slake containing citric acid to a first stage reactor, reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry, reacting the first partially converted calcium hydroxide calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide to produce a second partially converted calcium hydroxide calcium carbonate slurry, and reacting the second partially converted calcium hydroxide calcium carbonate slurry in a third stage reactor in the presence of carbon dioxide and fibrils to produce a filler-fiber composite.

In yet a further aspect, the present invention relates to a filler-fiber composite Including feeding slake containing citric acid to a first stage reactor, reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry, taking a first portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and reacting such in a second stage reactor in the

presence of carbon dioxide to produce a calcium carbonate/fibril composite to serve as a heel and taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and surfactant and reacting in the presence of CO₂ to produce a second partially converted Ca(OH)₂/CaCO₃/fibril material and reacting the second partially converted Ca(OH)₂/CaCO₃/fibril material in the presence of CO₂ in a third stage reactor to produce a filler-fiber composite.

In still a further aspect, the present invention relates to a filler-fiber composite including feeding slake containing citric acid to a first stage reactor, reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry, taking a first portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and reacting such in a second stage reactor in the presence of carbon dioxide to produce a calcium carbonate/fibril composite to serve as a heel and taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and polyacrylamide and reacting in the presence of CO₂ to produce a second partially converted Ca(OH)₂/CaCO₃/fibril material and reacting the second partially converted Ca(OH)₂/CaCO₃/fibril material in the presence of CO₂ in a third stage reactor to produce a filler/fiber composite.

In a final aspect, the present invention relates to a filler-fiber composite including feeding slake containing citric acid to a first stage reactor, reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a CaCO₃ heel and adding slake containing sodium bicarbonate to the heel material of the first stage reactor in the presence of CO₂ to produce

a partially converted calcium hydroxide calcium carbonate slurry and reacting the partially converted calcium hydroxide calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide and fibrils to produce a filler-fiber composite.

5 DETAILED DESCRIPTION OF THE INVENTION

Precipitation of PCC with Varying Morphologies

Continuous Flow Stir Tank Reactor (CFSTR)

Scalenohedral Morphology

The first step in this process involves making a high reactive $\text{Ca}(\text{OH})_2$ milk-of-lime slake and screening it at -325 mesh. This slake is then added to an agitated reactor, brought to a desired reaction temperature, 0.1 percent citric acid is added to the slake to inhibit aragonite formation, and reacted with CO_2 gas. The reaction proceeds 10 percent to 40 percent of the way through at which point the reaction is stopped. This produces a partially converted $\text{Ca}(\text{OH})_2$ / CaCO_3 slurry (approximately 20 percent solids by weight) which is then fed into a reaction vessel at a rate that matches CO_2 gassing to maintain a given conductivity (ionic saturation) to produce a scalenohedral crystal. This reaction proceeds until stabilization of the process is achieved. The product made once stabilization is achieved (approximately 95 percent converted) is then mixed with diluted fibrils (approximately 1.5 percent concentration) and water. This mixture is then reacted with CO_2 gas to endpoint pH 7.0. The product manufactured using this method can contain from about 0.2 percent to about 99.8 percent scalenohedral PCC with respect to fibrils at 3 percent to 5 percent total solids.

The product has a specific surface area from about 5 meters squared per gram to about 11 meters squared per gram; product solids from about 3 percent to about 5 percent and a PCC content from about 0.2 percent to about 99.8 percent, and is predominantly scalenohedral in morphology.

5 Aragonitic Morphology

The first step in this process involves making a high reactive $\text{Ca}(\text{OH})_2$ milk-of-lime slake and screened at -325 mesh. The concentration of this slake is approximately 15 percent by weight. This slake is then added to an agitated reactor, brought to a desired reaction temperature, from about 10 0.05 percent to about 0.04 percent additive is added to direct morphology and size, and reacted with CO_2 gas. The reaction proceeds 10 percent to 40 percent of the way through at which point the reaction is stopped. This produces a partially converted $\text{Ca}(\text{OH})_2 / \text{CaCO}_3$ slurry which is then fed into a reaction vessel at a rate that matches CO_2 gassing to maintain a given conductivity (ionic saturation) to produce an acicular, aragonitic crystal. The reaction continues until process 15 stabilization is achieved. The product made once stabilization is achieved, (approximately 95 percent calcium carbonate) is mixed with diluted fibrils (approximately 1.5 percent concentration) and water. The calcium carbonate and fibrils are then reacted with CO_2 gas to an endpoint of pH 7.0. The product manufactured using this method contains from about 0.2 percent to about 99.8 percent aragonitic PCC with respect to the fibrils at about 3 percent to about 5 percent total solids.

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The product has a specific surface area of about 5 meters squared per gram to about 8 meters squared per gram; product solids from about 3 percent to about 5 percent by weight and a PCC

content from about 0.2 percent to about 99.8 percent with respect to fibrils and has a predominantly aragonitic morphology.

Rhombohedral Morphology

5 The first step in this process involves making a high reactive $\text{Ca}(\text{OH})_2$ milk-of-lime slake which is screened at -325 mesh and has a concentration of approximately 20 percent by weight. 0.1 percent citric acid is added to inhibit aragonite formation. A portion of this slake is added to an agitated reactor, brought to a desired reaction temperature and carbonated with CO_2 gas. The reaction proceeds to conductivity minimum producing a "heel". A "heel" is defined as a fully
10 converted calcium carbonate crystal with average particle size typically in the range of about 1 micron to about 2.5 micron with any crystal morphology. Sodium bicarbonate is added to the remainder of the slake not used in the manufacture of the "heel" material. This slake and CO_2 is added to the "heel" material at a CO_2 gassing rate to maintain a given conductivity (ionic saturation) to produce a rhombohedral crystal. The reaction is continued until process stabilization is achieved.
15 Once stabilization is achieved, this product (approximately 90 percent to 95 percent converted) is mixed with diluted fibrils (approximately 1.5 percent concentration) and water. Additional CO_2 is added to an endpoint of pH 7.0. The product manufactured using this method contains from about 0.2 percent to about 99.8 percent rhombohedral PCC with respect to fibrils and is about 3 percent to about 5 percent total solids.

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The product has a specific surface area from about 5 meters squared per gram to about 8 meters squared per gram; product solids from about 3 percent to about 5 percent; and PCC content

from about 0.2 percent to about 99.8 percent and has a predominantly rhombohedral morphology:

EXAMPLES

The following examples are intended to exemplify the invention and are not intended to
5 limit the scope of the invention.

EXAMPLE 1

SCALENOHEDRAL PCC

Reacted 15 liters of water with 3 kilogram CaO at 50 degrees Celsius producing a 20 percent
10 by weight $\text{Ca}(\text{OH})_2$ slake. The $\text{Ca}(\text{OH})_2$ slake was then screened at -325 mesh producing a screened
slake that was transferred to a first 30-liter double jacketed stainless steel reaction vessel with an
agitation of 615 revolutions per minute (rpm). 0.1 percent citric acid, by weight of total theoretical
 CaCO_3 to be produced, was added to the screened slake in a 30-liter reaction vessel and the
temperature of the contents brought to 40 degrees Celsius. Began addition of 20 percent CO_2 gas in
15 air (14.83 standard liter minute CO_2 /59.30 standard liter minute air) to the 30-liter reaction vessel
to produce a 2:1 $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry. At this point, CO_2 gassing was stopped and the slurry was
transferred to an agitated 20-liter storage vessel.

2 liters of the 2:1 $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry was transferred to a first 4-liter agitated (1250 rpm)
20 stainless steel, double jacketed reaction vessel. The temperature was brought to 51 degrees Celsius
and 20 percent CO_2 gas in air (1.41 standard liter minute CO_2 /5.64 standard liter minute air) was
added to the first 4-liter reaction vessel until a pH of 7.0 was achieved producing a CaCO_3 slurry.

Once a pH 7.0 was achieved began addition of the 2:1 $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry of the 20-liter storage vessel to the first 4-liter reaction vessel while continuing to add 20 percent CO_2 gas in air (1.41 standard liter minute CO_2 /5.64 standard liter minute air) to the first 4-liter reaction vessel to maintain a conductivity of approximately 90 percent ionic saturation. The addition of $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry and CO_2 to the first 4-liter reaction vessel was continued for approximately 12 hours until product physical properties remained essentially unchanged, producing a CaCO_3 slurry that was approximately 98 percent converted. Transferred 0.18 liters of the 98 percent CaCO_3 slurry to a second 4-liter agitated (1250 rpm), stainless steel, double jacketed reaction vessel, added 0.66 liters of 3.8 percent by dry weight cellulosic fibers and diluted to 1.5 percent consistency. This mixture of CaCO_3 slurry and fiber was reacted with 20 percent CO_2 in air (1.41 standard liter minute CO_2 /5.64 standard liter minute air) to produce a CaCO_3 filler/fiber composite. The calcium carbonate filler had a predominantly scalenohedral morphology.

EXAMPLE 2

ARAGONITIC PCC

Reacted 10.5 liters of water with 2.1 kilograms CaO at 50 degrees Celsius producing a 15 percent by weight $\text{Ca}(\text{OH})_2$ slake. The $\text{Ca}(\text{OH})_2$ slake was then screened at -325 mesh producing a screened slake that was transferred to a 30-liter double jacketed stainless steel reaction vessel with an agitation of 615rpm. Added 0.1 percent by weight of a high surface area (HSSA) aragonitic seed (surface area ~40 meters squared per gram, approximately 25 percent solids) to the 30-liter reaction vessel and brought the temperature of the contents to 51degrees Celsius. A "seed" is defined as a fully converted aragonitic crystal that has been endpointed and milled to a high specific surface area

(i.e. greater than 30 meters squared per gram and typically a particle size of 0.1 to 0.4 microns).

Began addition of 10 percent CO₂ gas in air (5.24 standard liter minute CO₂/47.12 standard liter minute air) to the 30-liter stainless steel, double jacketed reaction vessel for a 15-minute period after which the CO₂ concentration was increased to 20 percent in air (10.47 standard liter minute

5 CO₂/41.89 standard liter minute air) for an additional 15 minutes producing a 2.3:1 Ca(OH)₂/CaCO₃ slurry. At which time CO₂ gassing was stopped. The 2.3:1 Ca(OH)₂/CaCO₃ slurry was transferred

to an agitated 20-liter storage vessel. Transferred 2 liters of the 2.3:1 Ca(OH)₂/CaCO₃ slurry to a first 4-liter agitated, double jacketed stainless steel reaction vessel with agitation set at 1250rpm and

the temperature was brought to 52 degrees Celsius. Began addition of 20 percent CO₂ gas in air

10 (1.00 standard liter minute CO₂/3.99 standard liter minute air) to the first 4-liter reaction vessel and the reaction was continued until a pH of 7.0 was achieved producing a 100 percent CaCO₃ slurry.

The temperature of the 100 percent CaCO₃ slurry of the first 4-liter reaction vessel was brought to 63 degrees Celsius. Began addition of the 2.3:1 Ca(OH)₂/CaCO₃ slurry of the 20-liter storage vessel

to the first 4-liter reaction vessel while continuing to add 20 percent CO₂ in air (1.00 standard liter

15 minute CO₂/3.99 standard liter minute air) to the first 4-liter reaction vessel maintaining a

conductivity of approximately 90 percent ionic saturation. Continued the reaction for approximately 9 hours until the physical properties of the resultant product remained essentially unchanged, producing a 98 percent by wt. CaCO₃ slurry.

20 Transferred 0.35 liters of the 98 percent CaCO₃ slurry to a second 4-liter agitated (1250 rpm), stainless steel, double jacketed reaction vessel, added 0.66 liters of 3.8 percent by wt. cellulosic fiber and 1.0 liters water to the second 4-liter reactor producing a 1.5 percent by wt. CaCO₃/fiber mixture.

Added an additional 20 percent CO₂ in air (1.00 standard liter minute CO₂/3.99 standard liter minute air) to the second 4-liter reaction vessel until a pH of 7.0 was reached at which time the reaction was completed producing a CaCO₃/fiber composite. The composite consisted of approximately 75 percent aragonitic PCC to fiber.

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EXAMPLE 3

RHOMBOHEDRAL PCC

Reacted 15 liters of water with 3 kilograms CaO at 50 degrees Celsius producing a 20 percent by weight Ca(OH)₂ slake. The Ca(OH)₂ slake was screened at -325 mesh producing a
10 screened slake that was transferred to an agitated 20-liter storage vessel. Transferred 2-liters of the screened slake from the 20-liter storage vessel to a first 4-liter agitated, stainless steel, double jacketed reaction vessel and began agitation at 1250rpm. Added 0.03 percent citric acid by weight of theoretical CaCO₃ to the first 4-liter reaction vessel and raised the temperature of the contents to 50 degrees Celsius. Added 20 percent CO₂ gas in air (1.44 standard liter minute CO₂/ 5.77 standard
15 liter minute air) to the first 4-liter reaction vessel until a pH of 7.0 was achieved producing a 100 percent CaCO₃ slurry. To the screened slake in the 20-liter storage vessel, added a solution of 1.3 percent by weight of Na₂CO₃, based on theoretical yield of CaCO₃, producing a Ca(OH)₂/ Na₂CO₃ slake. Increased the temperature of the contents of the first 4-liter reaction vessel to approximately 68 degrees Celsius and began addition of the Ca(OH)₂/ Na₂CO₃ slake of the 20-liter storage vessel
20 to the first 4-liter reaction vessel while continuing to add 20 percent CO₂ in air (1.44 standard liter minute CO₂/ 5.77 standard liter minute air) to the first 4-liter reaction vessel maintaining a conductivity of approximately 50 percent ionic saturation. Addition of the Ca(OH)₂/ Na₂CO₃ slake

and CO₂ was continued for approximately 12 hours until physical properties of the resultant product remained essentially unchanged producing an approximate 98 percent by wt. CaCO₃ slurry.

Transferred 0.22 liters of the 98 percent CaCO₃ slurry to a second 4-liter agitated (1250 rpm) dual jacketed, stainless steel reaction vessel and added 0.66 liters of 3.8 percent by weight cellulosic fiber and 1.0 liters water to the second 4-liter reactor producing a 1.5 percent by weight CaCO₃/fiber mixture. Added an additional 20 percent CO₂ in air (1.44 standard liter minute CO₂/5.77 standard liter minute air) to the second 4-liter reaction vessel until a pH of 7.0 was reached at which time the reaction was completed producing an approximate 3.4 percent by wt CaCO₃/fiber composite. The calcium carbonate had a predominantly rhombohedral morphology.

EXAMPLE 4

SCALENOHEDRAL - CFSTR

Reacted 15 liters of water with 3 kilograms CaO at 48 degrees Celsius to produce a Ca(OH)₂ slake, added an additional 6 liters of water producing a 20 percent by weight Ca(OH)₂ slake. The 20 percent Ca(OH)₂ slake was screened at -325 mesh and transferred to a 30-liter double jacketed, stainless steel reaction vessel with an agitation of 615rpm. Added 0.015 percent citric acid, by weight of total theoretical CaCO₃ to be produced, to the 30-liter reaction vessel and the temperature of the contents brought to 36 degrees Celsius. Began addition of 20 percent CO₂ gas in air (13.72 standard liter minute CO₂ / 54.89 standard liter minute air) to the 30-liter reaction vessel to produce a 5:1 Ca(OH)₂/CaCO₃ slurry. CO₂ gassing was stopped and the Ca(OH)₂/CaCO₃ slurry was transferred to an agitated 20-liter storage vessel.

In a 4-liter agitated storage vessel, combined 0.25 liters of the $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry with 0.66 liters of 3.8 percent by weight fibrils and with 1.09 liters of water making a $\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{fibril}$ material. Transferred 2 liters of the $\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{fibril}$ material to a 4-liter agitated (1250 revolutions per minute) reaction vessel and the temperature brought to 55 degrees Celsius and carbonated with 20 percent CO_2 in air (1.30 standard liter minute CO_2 / 5.23 standard liter minute air) to a pH of 7.0 producing a $\text{CaCO}_3/\text{fibril}$ composite. Prepared 16-liters of 1.5 percent by weight fibrils and a separate 10-liter vessel of water. To the 4-liter reaction vessel began addition of the $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ slurry of the 20-liter agitated storage vessel, along with the 1.5 percent consistency fibril mixture at 172.05 ml per minute, along with 31.21 ml per minute of additional water while maintaining the flow of CO_2 gas (1.30 standard liter minute CO_2 / 5.23 standard liter minute air) at a rate to maintain conductivity of approximately 90 percent ionic saturation, while maintaining mass balance of approximately 4 percent to 5 percent total solids.

This reaction was continued until product physical properties remained essentially unchanged. Addition of material from the storage vessel was stopped while CO_2 addition was continued and the material in the 4-liter agitated reaction vessel was brought to a pH of 7.0 at which time CO_2 addition was stopped producing a 2.2:1 $\text{CaCO}_3/\text{fibril}$ composite with the CaCO_3 having a well defined scalenohedral morphology.

EXAMPLE 5**SCALENOHEDRAL CFSTR/RECYCLE/SURFACTANT**

5 Reacted 15 liters of water with 3 kilograms CaO at 48 degrees Celsius to produce a Ca(OH)_2 slake, added an additional 6 liters of water producing a 20 percent by weight Ca(OH)_2 slake. The 20 percent Ca(OH)_2 slake was screened at -325 mesh and transferred to a 30-liter reaction vessel (615 revolutions per minute). Added 0.015 percent citric acid, by weight of total theoretical CaCO_3 to be produced, to the 30-liter reaction vessel and the temperature of the contents brought to 35
10 degrees Celsius. Began addition of 20 percent CO_2 gas in air (14.08 standard liter minute CO_2 / 56.30 standard liter minute air) to the 30-liter reaction vessel producing a 5:1 $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry. At this point, CO_2 gassing was stopped and the $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry was transferred to a 20-liter agitated storage vessel.

15 In a 4-liter agitated storage vessel, combined 0.25 liters of the $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry with 0.66 liters of 3.8 percent by weight fibrils and with 1.09 liters of water making 2 liters of $\text{Ca(OH)}_2/\text{CaCO}_3$ /fibril material.

20 Transferred 2 liters of the $\text{Ca(OH)}_2/\text{CaCO}_3$ /fibril material to a 4-liter stainless steel, double jacketed, agitated (1250 revolutions per minute) reaction vessel and the temperature was brought to 58 degrees Celsius. Reacted the $\text{Ca(OH)}_2/\text{CaCO}_3$ /fibril material with 20 percent CO_2 in air (1.30 standard liter minute CO_2 / 5.23 standard liter minute air) to a pH of 7.0.

At this point, prepared 16-liters of 1.5 percent by weight fibrils (6.32 liters of fibrils at 3.8 percent consistency and 9.68 liters of water) and a separate 10-liter vessel of water. Added 0.04 percent surfactant based on the volume of fibers at 1.5 percent consistency.

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Once a pH of 7.0 was achieved in the 4-liter reaction vessel, began addition of the remaining 5:1 $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry from the 20-liter agitated storage vessel, with a flow of the 1.5 percent fibril mixture at 176.48 ml per minute and with 32.00 ml per minute water from the 10-liter vessel to the 4-liter reaction vessel while maintaining the flow of CO_2 gas (1.30 standard liter minute CO_2 / 5.23 standard liter minute air) at a rate to maintain conductivity of approximately 90 percent ionic saturation, while maintaining mass balance of approximately 4 percent to 5 percent total solids. Continued addition of the material from the agitated storage vessel to the reaction vessel until product physical properties remained essentially unchanged. At which point, addition of material from the storage vessel was stopped while CO_2 addition was continued to a pH of 7.0 at which time CO_2 addition was stopped. This produced a 2.33:1 CaCO_3 /fibril composite with the calcium carbonate having a well defined scalenohedral morphology.

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EXAMPLE 6

SCALENOHEDRAL CFSTR/POLYACRYLAMIDE

Reacted 15 liters of water with 3 kilograms CaO at 48 degrees Celsius producing a Ca(OH)_2 slake, added an additional 6 liters of water producing a 20 percent by weight Ca(OH)_2 slake. The 20 percent Ca(OH)_2 slake was then screened at -325 mesh producing a screened slake that was

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transferred to a 30-liter agitated (615rpm) reaction vessel. Added 0.1 percent citric acid, by weight of total theoretical CaCO_3 to be produced, to the 30-liter reaction vessel and the temperature of the contents brought to 50 degrees Celsius. Began addition of 20 percent CO_2 gas in air (15.01 standard liter minute CO_2 / 60.06 standard liter minute air) to the 30-liter reaction vessel producing a 5:1
5 $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry. CO_2 gassing was stopped and the slurry was transferred to a 20-liter agitated storage vessel. To a 4-liter agitated vessel added 0.31 liters of the $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry, 0.60 liters of fibrils at 3.8 percent consistency and 1.09 liters of water to produce a $\text{Ca(OH)}_2/\text{CaCO}_3/\text{fibril}$ material. 2 liters of the $\text{Ca(OH)}_2/\text{CaCO}_3/\text{fibril}$ material was transferred to a 4-liter agitated (1250 revolutions per minute) reaction vessel and the temperature was brought to 51 degrees Celsius.
10 Began addition of 20 percent CO_2 in air (1.34 standard liter minute CO_2 / 5.34 standard liter minute air) until a pH of 7.0 was reached producing a $\text{CaCO}_3/\text{fibril}$ composite.

At this point, prepared 16-liters of 1.5 percent by weight fibrils (6.32 liters of fibrils at 3.8 percent consistency and 9.68 liters of water) and a separate 10-liter vessel of water. Added 0.05
15 percent cationic polyacrylamide (Percol 292) based on the volume of fibrils at 1.5 per cent consistency.

Once a pH of 7.0 was achieved in the 4-liter reaction vessel, began addition of the remaining 5:1 $\text{Ca(OH)}_2/\text{CaCO}_3$ slurry from the 20-liter agitated storage vessel, with a flow of the 1.5 percent
20 fibril mixture at 90 ml per minute, along with 48.5 ml per minute of additional water to the 4-liter agitated, double jacketed reaction vessel while maintaining the flow of CO_2 gas (1.30 standard liter minute CO_2 / 5.23 standard liter minute air) at a rate to maintain conductivity level of approximately

90 percent ionic saturation, and maintain mass balance of the reaction to maintain product concentration at approximately 4 percent to 5 percent solids. Continued addition of the material from the agitated storage vessel to the reaction vessel until product physical properties remained essentially unchanged. Addition of material from the 20-liter storage vessel was stopped while CO₂ addition was continued until a pH of 7.0 was reached at which time CO₂ addition was stopped producing a 3.34:1 CaCO₃/fibril composite with the PCC having a well defined scalenohedral morphology.

DEFINITION OF FIBRIL

A fibril is produced by refining (any pulp refiner known in the pulp processing industry) cellulose and/or mechanical pulp fiber. The fibrils are typically 0.1 to 2 microns in thickness and 10 to 400 microns in length and are additionally prepared according to U.S. Pat. 6,251,222, which is by this reference incorporated herein.

The control fiber of the present invention was refined at the Empire State Paper Research Institute (ESPRI) using an Escher-Wyss (conical) refiner to an 80° SR (freeness). Measured by a fiber quality analyzer (using arithmetic means) the control fibril measured 200-400 microns

HOW CONTROL FILLER/FIBER WAS MADE

Produce a 15% solids slake and mix with fibrils (~1.5% consistency) React in the presence of CO₂ to endpoint of pH of 7.0 producing a filler/fiber composite with a surface area of 6-11 m²/g (~60 to 80% PCC but can have more or less in composite)

TABLE 1***Breaking Length Physical Properties in Meters***

Filler Loading Levels	Scalenohedral Filler/Fiber	Aragonitic Filler/Fiber	Rhombohedral Filler/Fiber	Control Filler/Fiber
20	4,021	4,599	4,312	4,245
25	3,799	4,358	3,813	3,715
30	3,280	3,674	3,871	2,998

TABLE 2***Tensile Strength Physical Properties in kN/m***

Filler Loading Levels	Scalenohedral Filler/Fiber	Aragonitic Filler/Fiber	Rhombohedral Filler/Fiber	Control Filler/Fiber
20	3.062	3.555	3.397	3.382
25	3.124	3.324	2.999	3.021
30	2.658	2.785	3.005	2.448

TABLE 3***Internal Bond Strength Physical Properties in ft-lb***

Filler Loading Levels	Scalenohedral Filler/Fiber	Aragonitic Filler/Fiber	Rhombohedral Filler/Fiber	Control Filler/Fiber
20	237.70	264.07	283.13	255.67
25	263.20	285.95	251.65	256.95
30	242.63	248.60	273.65	249.53

The morphology controlled filler/fiber composite showed equivalent or greater physical properties (i.e. tensile strength, breaking length, and internal bond strength) as compared with the control filler/fiber.

TABLE 4***ISO Opacity Optical Properties***

<i>Filler Loading Levels</i>	<i>Scalenohedral Filler/Fiber</i>	<i>Aragonitic Filler/Fiber</i>	<i>Rhombohedral Filler/Fiber</i>	<i>Control Filler/Fiber</i>
20	89.20	88.20	87.38	88.18
25	89.93	89.15	88.78	89.55
30	90.95	90.40	89.68	90.83

TABLE 5***Pigment Scatter Optical Properties***

<i>Filler Loading Levels</i>	<i>Scalenohedral Filler/Fiber</i>	<i>Aragonitic Filler/Fiber</i>	<i>Rhombohedral Filler/Fiber</i>	<i>Control Filler/Fiber</i>
20	60.15	55.47	55.08	58.55
25	64.90	62.40	61.10	65.40
30	70.55	69.55	65.80	73.13

The morphology controlled filler/fiber composite showed equivalent optical properties (i.e. ISO Opacity and Pigment Scatter) as compared with the control filler/fiber.

We claim:

1. A filler-fiber composite comprising:

(a) feeding slake containing citric acid to a first stage reactor

(b) reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry

(c) reacting the first partially converted calcium hydroxide calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide to produce a second partially converted calcium hydroxide calcium carbonate slurry and

(d) reacting the second partially converted calcium hydroxide calcium carbonate slurry in a third stage reactor in the presence of carbon dioxide and fibrils to produce a filler-fiber composite.

2. The filler-fiber composite of claim 1 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

3. The filler-fiber composite of claim 2 wherein the filler is scalenohedral having a specific surface area of from about 5 meters squared per gram to about 11 meters squared per gram.

4. The filler-fiber composite of claim 3 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.
5. The filler-fiber composite of claim 4 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.
6. The filler-fiber composite of claim 5 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.
7. A method for producing a filler-fiber composite comprising:
 - (a) feeding slake containing citric acid to a first stage reactor
 - (b) reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry
 - (c) reacting the first partially converted calcium hydroxide calcium carbonate slurry in a second stage reactor in the presence of carbon dioxide to produce a second partially converted calcium hydroxide calcium carbonate slurry and
 - (d) reacting the second partially converted calcium hydroxide calcium carbonate slurry in a third stage reactor in the presence of carbon dioxide and fibers to produce a filler-fiber composite.

8. The method of producing the filler-fiber composite of claim 7 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

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9. The method of producing the filler-fiber composite of claim 8 wherein the filler is scalenohedral and has a specific surface area of from about 5 meters squared gram to about 11 meters squared per gram.

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10. The method of producing the filler-fiber composite of claim 9 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.

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11. The method of producing the filler-fiber composite of claim 10 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.

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12. The filler-fiber composite of claim 11 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.
13. The filler-fiber composite of claim 1 utilized in paper or paperboard
14. The filler-fiber composite of claim 7 utilized in paper or paperboard.
15. The paper produced utilizing the filler-fiber of claim 1.

16. The paper produced utilizing the filler-fiber of claim 7.

17. A filler-fiber composite comprising:

(a) feeding slake containing citric acid to a first stage reactor

(b) reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry

(c) taking a first portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and reacting such in a second stage reactor in the presence of carbon dioxide to produce a calcium carbonate/fibril composite to serve as a heel and

(d) taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and surfactant and reacting in the presence of CO₂ to produce a second partially converted Ca(OH)₂/CaCO₃/fibril material and

(e) reacting the second partially converted Ca(OH)₂/CaCO₃/fibril material in the presence of CO₂ in a third stage reactor to produce a filler-fiber composite.

18. The filler-fiber composite of claim 17 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

19. The filler-fiber composite of claim 18 wherein the filler is scalenohedral having a specific surface area of from about 5 meters squared per gram to about 11 meters squared per gram.

5 20. The filler-fiber composite of claim 19 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.

10 21. The filler-fiber composite of claim 20 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.

22. The filler-fiber composite of claim 21 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.

15 23. A method for producing a filler-fiber composite comprising:

(a) feeding slake containing citric acid to a first stage reactor
(b) reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry

20 (c) taking a first portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and reacting such in a second stage reactor in the

presence of carbon dioxide to produce a calcium carbonate\fibril composite to serve as a heel and

- (d) taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and surfactant and reacting in the presence of CO₂ to produce a second partially converted Ca(OH)₂/CaCO₃/fibril material and reacting the second partially converted Ca(OH)₂/CaCO₃/fibril material in the presence of CO₂ in a third stage reactor to produce a filler-fiber composite.

24. The method for producing filler-fiber composite of claim 23 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

25. The method for producing filler-fiber composite of claim 24 wherein the filler is scalenohedral having a specific surface area of from about 5 meters squared per gram to about 11 meters squared per gram.

26. The method for producing filler-fiber composite of claim 25 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.

27. The method for producing filler-fiber composite of claim 26 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.

5 28. The method for producing filler-fiber composite of claim 27 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.

29. The filler-fiber composite of claim 17 utilized in paper or paperboard

30. The filler-fiber composite of claim 23 utilized in paper or paperboard.

10 31. The paper produced utilizing the filler-fiber of claim 17.

32. The paper produced utilizing the filler-fiber of claim 23.

33. A filler-fiber composite comprising:

(a) feeding slake containing citric acid to a first stage reactor

(b) reacting the slake containing citric acid in the first stage reactor in the presence of

15 carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry

(c) taking a first portion of the partially converted calcium hydroxide calcium

carbonate slurry adding fibrils and reacting such in a second stage reactor in the

presence of carbon dioxide to produce a calcium carbonate/fibril composite to serve

20 as a heel and

- (d) taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and polyacrylamide and reacting in the presence of CO_2 to produce a second partially converted $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ /fibril material and
- (e) reacting the second partially converted $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ /fibril material in the presence of CO_2 in a third stage reactor to produce a filler/fiber composite.

34. The filler-fiber composite of claim 33 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

35. The filler-fiber composite of claim 34 wherein the filler is scalenohedral having a specific surface area of from about 5 meters squared per gram to about 11 meters squared per gram.

36. The filler-fiber composite of claim 35 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.

37. The filler-fiber composite of claim 36 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.

38. The filler-fiber composite of claim 37 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.

39. A method of producing a filler-fiber composite comprising:

5 (a) feeding slake containing citric acid to a first stage reactor

(b) reacting the slake containing citric acid in the first stage reactor in the presence of carbon dioxide to produce a first partially converted calcium hydroxide calcium carbonate slurry

10 (c) taking a first portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and reacting such in a second stage reactor in the presence of carbon dioxide to produce a calcium carbonate/fibril composite to serve as a heel and

(d) taking a second portion of the partially converted calcium hydroxide calcium carbonate slurry adding fibrils and polyacrylamide and
15 reacting in the presence of CO₂ to produce a second partially converted Ca(OH)₂/CaCO₃/fibril material and

(e) reacting the second partially converted Ca(OH)₂/CaCO₃/fibril material in the presence of CO₂ in a third stage reactor to produce a filler/fiber composite.

20 40. The method for producing filler-fiber composite of claim 39 wherein the fiber is from about 0.1 microns to about 2 microns in thickness and from about 10 microns to about 400 microns in length.

41. The method for producing filler-fiber composite of claim 40 wherein the filler is scalenohedral having a specific surface area of from about 5 meters squared per gram to about 11 meters squared per gram.

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42. The method for producing filler-fiber composite of claim 41 wherein the calcium hydroxide calcium carbonate slurry is converted from about 20 percent to about 40 percent.

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43. The method for producing filler-fiber composite of claim 42 wherein the first partially converted calcium hydroxide calcium carbonate slurry is converted from about 41 percent to about 99 percent.

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44. The method for producing filler-fiber composite of claim 43 wherein the second partially converted calcium hydroxide calcium carbonate slurry is converted to a filler-fiber composite.

45. The filler-fiber composite of claim 33 utilized in paper or paperboard

46. The filler-fiber composite of claim 39 utilized in paper or paperboard.

47. The paper produced utilizing the filler-fiber of claim 33.

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48. The paper produced utilizing the filler-fiber of claim 39.