FINAL REPORT

Project Title: Fibrous Fillers to Manufacture Ultra High Ash/Performance Paper

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List of Definitions

Fibrous Fillers: Catch-all name for all the various forms of calcium silicates that GRI can generate.

S-PCC: Trade name for GRI's precipitated calcium carbonate made using high speed pressure carbonation.

Flue Gas: Greenhouse gases containing CO₂ coming out of a smoke stack from a boiler or lime kiln where combustion occurs.

Porosity: A measure of the ease with which a fluid (gas or liquid) passes through a solid material.

Waterglass: Common name for Sodium Silicate (Na₂SiO₃)

Bulk Temperature: The temperature at which most of the reaction takes place during the manufacturing of Fibrous Fillers

Brightness: The amount of light at 526 nm that is reflected back from a sheet of paper or pigment

Opacity: The ability for a sheet of paper to block light from passing through it

Tensile: The amount of force necessary to rip a sheet of paper by pulling on the ends of the paper

Stiffness: The ability of paper to resist bending under the influence of a bending force

Water Absorption: Pigment property that measures the maximum amount of water necessary to take dry powder and have it stay in a solid (gel) phase.

Calcium / Silica Molar Ratio: (Molar Ratio) The ratio of the number of calcium moles to the number of silica moles in a silicate.

X-Ray Diffraction: (XRD) The ability of crystal phases to reflect X-rays at certain angles. Intrinsic property of pigments.

SEM: Scanning Electron Microscope. Pictures taken using a sophisticated electron microscope to see structure in the micron and nanometer scale

DE: Diatomaceous Earth. A silica source made from mined deposits of coral that is separated and calcined with sodium to give high brightness. Contains Cristobalite

Quartz: Mined source of silica.

Lime: Calcium Hydroxide or Ca(OH)₂. Raw material used to make both Fibrous Fillers and S-PCC. Made from the reaction of quicklime (CaO) with water.

Surface Area: The extent of the surface that defines a volume.

Nano-scale: 1 billionth of a meter

Micro-scale: 1 millionth of a meter

Burst Strength: The ability of paper to resist rupture when exposed to a force perpendicular to its face.

Slaking: The reaction of quicklime and water to make lime

Quicklime: Calcium Oxide (CaO) made by heating limestone to 900 °C to convert the CaCO₃ into CaO for shipping. Reacts exothermically with water.

Carbonation: The reaction of lime with carbon dioxide (CO₂) to make Precipitated Calcium Carbonate

PCC: Precipitated Calcium Carbonate. Calcium Carbonate made by the reaction of lime with CO₂ in an open vessel.

S-PCC SC: Scalenohedral form of S-PCC

S-PCC RH: Rhombohedral form of S-PCC

S-PCC AR: Aragonite form of S-PCC

SNF: Foshagite, Tech – 8, or T8: Calcium Silicate made using high heat and high Ca/Si molar ratio. Characterized by long, thin fiber-like structures that have very high aspect ratios

SMP: Riversideite, Tech – 4, or T4: Calcium Silicate made using medium heat and low Ca/Si molar ratio. Characterized by large globules of unseparated fibers

SMP-LDD: Tobermorite, Tech – 6, or T6: Calcium Silicate made using medium heat and medium Ca/Si molar ratio. Characterized by small plate-like globules of unseparated fibers

SMF: Xonotlite, Tech – 7, or T7: Calcium Silicate made using high heat and medium Ca/Si molar ratio. Characterized by short, thin fiber-like structures that have medium aspect ratios

Slurry Solids: The solids portion (mass fraction) of the product slurry

Waterglass: Trade name for Sodium Silicate

Handsheet: a small circle or square of paper made using a mold and then pressed and dried. Used to quickly test paper properties without expensive equipment or time requirements

AF&PA: American Forest and Paper Association, an industry association.

EXECUTIVE SUMMARY

Background: The paper industry is one of the largest users of energy and emitters of CO₂ in the US manufacturing industry. In addition to that, it is facing tremendous financial pressure due to lower cost imports. The fine paper industry has shrunk from 15 million tons per year production to 10 million tons per year in the last 5 years. This has resulted in mill closures and **job losses**. The AF&PA and the DOE formed a program called Agenda 2020 to help in funding to develop **breakthrough** technologies to provide help in meeting these challenges.

GR International: GRI had already developed several transformational technologies as described below:

- Silicate Nano-Fibers (US Patent # 6,726,807). These are produced by a hydrothermal reaction between an alkaline metal oxide (such as CaO) and a silica source. The process variables are calcium silica ratio, reaction temperature, slurry solids concentration, and impeller speed. By changing these variables, we can change the phases of calcium silicate, such as Silicate Nano-Fiber (Foshagite), Silicate Macro Particles (Riversideite), Silicate Macro Particles – Low Dryer Demand (Tobermorite), and Silicate Macro Fibers (Xonotlite) (See figures a, b, c, & d). Key quality measures for these silicates are surface area, pH, particle size, and brightness. The key performance characteristics for paper were the sheet bulk, optical, porosity, and strength properties.
- Pressurized CO₂ Capture Technology to produce Super – Precipitated Calcium Carbonates (US Patent # 6,251,356). S-PCC is manufactured by reacting CO₂ with an alkaline metal oxide like CaO under subcritical pressure. The pressure carbonation significantly increases the reaction kinetics of the carbonation reaction from 1 g/L/min to 6 g/L/min – a 600 % increase. Other process variables affecting reaction kinetics and morphology of S-PCC are reaction temperature, CaO concentration, impeller tip speed and CO₂ concentration (See figures e & f). Key quality measures for S-PCC are surface area, reaction rate, particle size, and brightness. The key performance characteristics for paper are the sheet bulk, optical, and strength properties.
- Common Manufacturing Equipment to produce the above mentioned products (US Patent # 7,048,900). This technology involves a specially designed **pressure reactor** and accompanying equipment to produce both **Silicate Nano-Fibers** and **Super-Precipitated Calcium Carbonates** in the same reactor.

DOE Grant DE-FC07-013ID14439: GRI was awarded a \$ 3.0 million grant under DE-FC07-013ID14439 from Agenda 2020 to optimize, scale-up, and commercialize it's technologies for application in paper.

Project Title: **Fibrous Fillers to Manufacture Ultra High Ash / Performance Paper**

Objectives: The objectives of this project were:

- To optimize and scale-up Fibrous Fillers technology, ready for commercial deployment
- To develop ultra high ash / high performance paper using Fibrous Fillers.

Goal: The goal was to reduce **energy consumption, carbon footprint, and cost of manufacturing** paper and related industries.

Technical Highlights

Task I: Pigment Optimization

1. **Lab Scale Empirical Process Modeling / Optimization for Silicate Nano-Fibers:** A statistically designed experiment was carried out to model the key process variables such as reactor temperature, impeller speed, calcium / silica ratio, and slurry solid concentration. The resulting calcium silicate hydrates were tested for particle size, X-Ray diffraction patterns, and BET surface area. The pigment was used to make paper. The paper handsheets were tested for key paper properties. The result of the study showed that, for example, **opacity increased with increasing reaction temperature and reaction solids**. It also showed increases with the calcium / silica ratio and impeller speed reduced the opacity.
2. **Raw Material Studies:**
 - a. Alternative silica sources were evaluated. The results indicated that the current Diatomaceous Earth performed well. However, it was possible to make Silicate Nano-Fibers using either **Quartz** or **Sodium Silicate**.
 - b. Alternative lime sources were tested. The result confirmed that both Mississippi and Graymont limes were acceptable to produce good quality Silicate Nano-Fibers.
3. **New Product Development:** The SMP product gave very high sheet bulk (+ 25 %) and stiffness (+ 100 %), but it was difficult to remove water from it and thus hard to dry. By changing the process conditions, such as calcium / silica ratio, slurry solids, and reaction temperature, we were able to produce a product with lower surface area that dewater to a higher solids (6 – 7 %) and thus required less energy to dry. We later undertook a statistically designed experiment to further optimize SMP-LDD.
4. **Pilot Scale Development (30 gallon high pressure reactor):** The research was moved from a 2 gallon lab reactor to a 30 gallon high pressure (1000 psig) reactor. Optimum process conditions from the 2 gallon reactor were employed to make batches in a 30 gallon reactor. The test results showed that the SNF quality was similar to the SNF from the 2 gallon reactor. More importantly, the handsheets data confirmed that SNF made in both the 2 gallon and 30 gallon reactors gave 2.0 points higher opacity than standard PCC. This confirms that the scale-up from the lab (2 gallon) to pilot (30 gallon) was valid. Several other optimization studies were carried out confirmed the robustness of the process of manufacturing Silicate Nano-Fibers.
5. **Commercial Scale Production of SMP using a rented (Toll Manufacturer) Plant:** In this toll manufacturing plant, there were significant differences in the raw materials such as lime and DE as well as the process itself. The result was that the silicates produced were significantly different. The product also did not perform well in the paper handsheet evaluation. At this stage, the decision was made to **build our own prototype commercial plant** at Grays Harbor Paper Mill location.
6. **Prototype Commercial Plant Scale-Up:** Between Q4, 2005 and Q1, 2006 the prototype plant was built (See Figure h). This was to further demonstrate the validity of SNF manufacturing process. This reactor, however, had a maximum pressure rating to 220 psig and 200 °C. Thus, it could produce only Silicate Macro Particles (SMP) and not Silicate Nano-Fibers (SNF), which required higher temperatures and pressures.

7. **Direct comparison of the lab (2 gallon), pilot (30 gallon) and prototype (5,000 gallon) reactors:** Reactions were carried out in all three reactors under identical process conditions to produce Silicate Macro Particles or SMP. The three products were tested by X-Ray diffraction, SEM, and particle size. The results showed that the three products were identical. The X-Ray diffraction pattern characteristic of SMP is Riversideite. Samples are given in Figure i. This conclusively proved that the scale-up process to manufacture Silicate Macro Particles was successful.
8. **Super-Precipitated Calcium Carbonate (S-PCC):** Statistically designed experiments were carried out to correlate the key S-PCC process conditions with:
 - a. S-PCC product attributes and
 - b. key paper properties.

The statistical analysis of the results and the mathematical models made confirmed that:

- a. **reaction rate** was highly dependent on the square of the **reaction pressure**,
- b. **surface area** had a linear relationship with reaction temperature, and
- c. **opacity**, which is a function of surface area, also directly correlated with **reaction temperature**.

This model was then validated from the **lab to the pilot and then the commercial scale reactors**.

Task II: Mechanism of Formation of Silicate Nano-Fibers

Lawrence Livermore National Laboratory, under contract with GRI, conducted several experiments to elucidate the reaction mechanism of Silicate Nano-Fiber formation. The LLNL key finding was **the reaction between silica and lime goes through a gel formation with high surface area (157 m²/g). Upon further addition of energy, the high surface area gel grows into low surface area (20 m²/g) Fibrous Fillers**. However, LLNL was not able to repeat the formation of SNF, mainly due to the difference in pressure reactors.

Task III: Making Ultra High Ash / High Performance Paper

1. **Ultra High Ash Handsheets:** Statistically designed experiments were carried out to produce ultra high ash (45 % filler level) paper using a combination of Silicate Macro Particles (SMP), Silicate Nano-Fibers (SNF), and market PCC. The key findings from the polynomial models were that **SMP gave the highest bulk and stiffness while SNF produced the best optical properties, porosity, and smoothness**. Also there were significant synergistic interactions between the three pigments as the ash levels were increased from 15 % to 30 % to 45 % filler (See figure j). Finally, it was fully demonstrated that the ash level can be increased from 15 % to 45 % using silicates, while maintaining key paper properties equal or better to 15 % PCC sheets.
2. **Energy Efficiency:** The effect of GRI's various silicates (SMP, SNF) and S-PCC were tested for their impact on energy consumption in paper drying process. Handsheets containing various GRI pigments and market PCC were passed through a roll press 3 times consequently. The solids after each pass were determined experimentally. The results indicated that S-PCC could be pressed to 10 % higher solids than market PCC. **The potential savings in the drying energy can be as high as 40 %.**
3. **Commercial Paper Machine Trials:** Paper machine trials were conducted using S-PCC, SMP, and Silicate Macro Fibers produced in the full scale prototype plant. Some key highlights are given below.

- a. S-PCC trial showed that it performed equal or better than market PCC. S-PCC significantly reduced the steam demand (energy)
- b. Combinations of SMP and Silicate Macro Fibers were able to demonstrate the following:
 - i. Reduction in basis weight by introducing silicate products to make an 18.5 # sheet with matching properties of a 20 # sheet containing market PCC.
 - ii. At equal basis weight, the paper gave 20 % higher bulk and 25 % higher stiffness.
 - iii. Increase in ash level paper by adding 5 % Fibrous Fillers to give higher optical properties while maintaining most of the other key paper properties.

Task IV: Surface Coating Application of Silicate Nano-Fibers

Western Michigan University, under a research contract with GRI, carried out a study for application of Silicate Nano-Fibers in surface coating and compared the result to more expensive products such as Optisil and Fumed Silica. The results showed that the Silicate Nano-Fibers gave **equal or better brightness, smoothness, and gloss** than the more expensive pigments.

Task V: Silicate – Pulp Fiber Interactions

This task could not be undertaken due to lack of funding.

Key Project Milestones

Some of the key milestones of this program can be summarized as:

- Process optimization for manufacturing various calcium silicate Fibrous Fillers
- Scale-up of manufacturing from lab (2 gallon) to pilot (30 gallon) to, finally, full scale prototype (5,000 gallon).
- Manufacture of Ultra High Ash Paper with up to 45 % filler, thus increasing the ash level from current average of 15 % PCC to 45 % ash consisting of a combination of Fibrous Fillers and Precipitated Calcium Carbonates
- Successful commercial paper machine trials
- Market acceptance of silicate containing paper

Value Propositions

The key value propositions arising out of this program can be summarized as the following:

1. reduction in basis weight,
2. replacement of pulp fibers with Silicate Nano-Fibers (ultra high ash),
3. reduction in energy consumption, and
4. carbon capture by pressure carbonation.

Commercial Validation

According to a non-integrated mill, they have realized savings of up to \$ 18 / ton of cut size paper. A fully integrated mill reported potential savings in the range of \$ 10-14 / ton.

In short, GRI was able to meet the key project objectives as agreed upon with the DOE.

Budget

1. GRI finished the project under the DOE's budget.

2. The applicant and its industrial partners contribution was \$ 1,833,222, which was 50 % above the minimum 40 % required.

Next Steps

- Commercialization of the Silicate Nano-Fiber and S-PCC technologies.
- Second generation technology development (Wollastonite)
- Application of Fibrous Fillers in non-paper areas like paints, plastics, ceramics, and glass.
- Application of carbon capture technology in power plants, cement plants, and refineries to capture CO₂ and produce value added products.

Figure 1: Lab Scale SMP

Figure 2: Pilot Scale SMP

Figure 3: Commercial Scale SMP

Figure i: XRD Diagrams showing XRD diffraction patterns for SMP made in the lab, pilot, and commercial reactors.

Figure j: Stiffness response at 45 % ash

BACKGROUND:

- **Industry Needs**

The paper industry was faced with escalating **costs** of manufacture, shrinking margins, and challenges to reduce **energy consumption** and **environmental load**. The industry needed a breakthrough technology solution to meet these challenges.

- **Agenda 2020**

The DOE in partnership with paper industry leaders formed “Agenda 2020” to streamline the approval and implementation of new, breakthrough technologies to help meet the paper industry’s needs. As part of this program, GRI was awarded a \$ 3.0 grant with agreements from the industry to provide about 20 % cash or in-kind support.

- **GRI’s Solution**

- a) **Fibrous Fillers**

GRI had developed a series of calcium and silica based fillers, collectively referred to as “**Fibrous Fillers**”. They have been patented (US #: 6,726,807). These products shared similar properties, such as low bulk density and a large secondary particle size. It was the primary structure, however, which sets our two products apart. The first product, Silicate Nano-Fibers (SNF), consisted of long, thin, needle-like “nano-fibers” with aspect ratios between 50:1 and 100:1, joined together into spherical agglomerates. The second was referred to as silicate macro-particles (SMP) characterized by a series of nano particles intergrowths formed into a continuous, globular structure. The unique product attributes of SNF provided much improved **optical properties** with minimal strength loss, while SMP provided exceptional **sheet bulk** with higher strength and **stiffness**. The combination of these fillers imparted superior paper properties, which include improvements in sheet bulk, smoothness, porosity, stiffness, brightness and opacity, simultaneously. These “Fibrous Fillers” had also been shown to outperform conventional fillers at equivalent and higher usage levels.

- b) **Engineered Super Precipitated Calcium Carbonates**

GRI had also developed a novel process for the manufacture of Super – Precipitated Calcium Carbonates (S-PCC).

- **GRI’s Approach**

GRI had already succeeded in producing these pigments in **lab** and **pilot scale**. It had also demonstrated their unique performance attributes in paper. Our recent focus was 1) build a **prototype plant** for manufacturing of “Fibrous Fillers” on a commercial scale reactor (US Patent #: 7,048,900), the application of “Fibrous Fillers” in paper (proof of concept), 2) to increase the fundamental knowledge of pigment manufacturing and 3) to run commercial paper machine trials. With this in view, our approach was to run a parallel program consisting of the following tasks:

- a) To optimize the fillers preparation at the lab and pilot scale,
 - b) to scale up production of “Fibrous Fillers” to commercial scale – prototype plant,
 - c) to evaluate the performance of “Fibrous Fillers” on a commercial paper machine; and
 - d) to study the reaction mechanisms of pigment preparations and interactions.
 - e) to study the mechanism of pulp and fibrous filler interaction

GRI had entered into an agreement with another pigment manufacturer to carry out experiments necessary to scale up the manufacturing of “Fibrous Fillers” from GRI’s 30 gallon pilot reactor to

a full commercial scale, 5,000 gallon reactor. The material produced from the full scale reactor was used for production scale paper machine trials. These trials were conducted with our industry partners like Grays Harbor Paper Company and Weyerhaeuser Company.

PROJECT OBJECTIVE (FY03): To verify the techno-economic viability of manufacturing GRI's novel calcium silicate "Fibrous Fillers" in paper industry.

- I) To optimize and scale-up novel "Fibrous Fillers" and S-PCC
- II) The other objectives of this project were to apply these novel fillers for the following:
 - a) to manufacture a paper composite where up to 40 - 50% natural fiber is replaced with calcium and silica based pigments ("Fibrous Filler") and S-PCC;
 - b) to reduce the cost of production of paper;
 - c) to reduce environmental load in the paper mill; and
 - d) to reduce overall energy consumption.
 - e) to produce value-added paper products;

Additional Project Objective (FY 04): Based on input from the DOE/AF&PA Review Team, we have added yet another objective. This was to develop a low cost calcium silicate, which would cost equal to, or lower than, pulp delivered to the headbox (~ \$300/ton).

Additional Project Objective (FY 04): In order to meet the main objective we needed to build a prototype plant to manufacture "fibrous fillers" (producing large quantities of fibrous fillers for commercial trials).

Focus For FY 05, FY06, FY07, and FY08: Validation of Technology on a Commercial Scale

- GRI's primary focus was to operate a prototype plant for production of fibrous fillers and conduct commercial scale paper trials followed by market evaluation of experimental paper.
- GRI was also working with the University of Washington to study the mechanism of pulp and fibrous filler interaction.
- GRI was also scaling up the production of low-cost, energy efficient engineered filler modifications from our already patented S-PCC (Tech-2) (US Patent #: 6,251,356).

TASKS

The whole project was divided into the following tasks:

- I) Optimization and scale-up of "Fibrous Fillers" and S-PCC (task performed by GRI),
- II) Elucidate the mechanism of formation of "Fibrous Fillers" (contracted to Lawrence Livermore National Laboratory),
- III) Optimize application of fillers in paper wet-end (task performed by GRI),
- IV) Optimize application of fillers as a coating on the surface of paper (contracted to Western Michigan University), and
- V) Elucidate the mechanism of "Fibrous Filler" – paper interactions (contracted to University of Washington).

The main focus of this project was in tasks I and III. Tasks II and IV were concluded after the initial objectives were completed. Task V was eliminated due to lack of funding.

The final report is organized based on the tasks listed above as well as by year. Highlights of significant sub-tasks are discussed.

KEY ACCOMPLISHMENTS:

TASK I (GRI):

Optimization of Manufacture of Silicate Nano-Fibers (SNF) and Silicate Macro-Particle (SMP).

Task I.2.1 Process Modeling: Empirical process models and response surface analysis employing the technique of designed optimization experimentation (DOE) (FY 2004 Q1)

Objective:

To evaluate the effect of Calcium / Silica Molar Ratio, reaction temperature, slurry solids concentration, and agitator RPM on preparation of Tech – 8 and all paper properties – both physical and optical.

Experimental:

This was a 4 factor experiment at 2 levels. Three center points were run to detect curvature of the responses. This gave us a total of 11 runs. This is fractional factorial design (Resolution IV) - which means that all main effects were evaluated independently. Interactions were confounded with one another (see alias structure below). However, there were several statistical tools that can help evaluate interactions independently after the experiment. This was a randomized design. The table below outlines the experimental conditions. The responses for the experiment were all fibrous filler and paper properties. Results were evaluated in Minitab at the 90 percent confidence level.

Independent Variables

T = Temperature [=] °C

R = Impeller Speed [=] RPM

Ca/Si = Ca/Si Ratio [=] Molar Ratio

S = Reaction Solids Concentration [=] Pounds/Gallon

Dependent Variables:

1. Sheet opacity (normalized for basis) (ISO).
2. Sheet brightness (ISO).
3. Sheet bulk (cm³/g).
4. Sheet porosity (sec/100 mL air).
5. Sheet smoothness (Sheffield units).
6. Sheet tensile strength (N*m/g).
7. Sheet stiffness (mg).

Key Results, Analysis, and Discussions:

Fibrous Filler Properties

Particle Size Distribution. The mean particle size (d_{50}) of the secondary agglomerate of silicate nano-fiber varied from a low of 14.9 microns to a high of 35.8 microns depending upon the experimental conditions employed.

X-Ray Diffraction Analysis. The phase composition of silicate nano-fibers varied considerably. In most cases, the predominant phase, as desired, was Foshagite (with some other minor crystalline phases). However, in the experimental condition employed in reaction WX067 gave predominantly an amorphous phase with only some Foshagite.

Surface Area (m^2/g) (B.E.T. Method). The surface area of the SNF varied from a low of $\sim 6.27 m^2/g$ to a high of $21.34 m^2/g$, once again depending upon the experimental conditions employed.

In summary, the SNF product quality responded to variation in process conditions as expected.

Fibrous Filler Performance in Paper

These eleven batches of SNF were used to make handsheets at 15, 20 and 25% ash levels. The resulting sheets were conditioned, calendared and tested for various key paper properties like sheet opacity, brightness, scattering coefficient of the filler, bulk, porosity, smoothness, etc. The test data was interpolated to a 20% ash level.

Statistical Analysis of Data Using Minitab:

In this analysis, the process conditions employed to manufacture nano-fibers were correlated to SNF in paper resulting in mathematical models.

where the independent variables were as described above.

Main Effects: The effect of each above independent variable on fibrous filler quality, which in turn, affects normalized paper opacity are shown in Figure 1.

Figure 1: Opacity Response to Independent Variables

The other key findings were;

Sheet Porosity. Only rotation per minute of the agitator produced the most significant effect on sheet porosity.

Filler Scattering Coefficient “s”. According to the analysis, the process conditions which impact the sheet scattering coefficient/power of SNF were an interaction between temperature and concentration, as well as between temperature and calcium silica ratio. Concentration of slurry was found to be not significant.

Conclusion

By varying the process conditions, the crystal phase, surface area, and particle size distribution can be varied significantly. This, in turn, can significantly affect the paper properties.

Task I.2.1: Verify process models for 2.0-gallon reactor (FY 2004 Q2)

Objective:

To carry out experiments to a) verify the validity of process models developed last quarter and b) determine repeatability of process to manufacture silicate nano-fibers.

Experimental:

4 experiments were carried out with the 2-gallon reactor under identical conditions. The resulting SNF pigments were tested and their performance in paper were evaluated. The process conditions are given in Table 1.

Table 1: Process conditions for repeatability

Batch	Product	Silica Source
WX114	Tech-8	DE
WX125	Tech-8	DE
WX127	Tech-8	DE
WX128	Tech-8	DE

DE = Diatomaceous Earth

Key Results and Discussion

Fibrous Filler Properties

Calcium/Silica Molar Ratio. The ratio was fairly repeatable.

Water Absorption (Screened Powder-SNF). The data shows a range of 582% to 713% with a standard deviation of 59. These variations were due to the secondary structure of SNF particles and represent the limit of natural variation.

Brightness. The brightness of the SNF pigments were in a fairly close range of 92.8 to 93.8 reflecting a very repeatable process.

Dry Cake Appearance. . All 4 samples were found to be soft and bulky. This is an indirect sign of structure of Ca^{++} and SiO_2^{--} chain structure.

Fibrous Filler Performance in Paper.

The performance of the four sets of pigments were evaluated by using them in paper (handsheets). The results of the testing of handsheets are given in Table 3 in FY 2004 Q2. Some of the key paper properties of the pigments are discussed below.

Sheet Bulk. The resulting sheet bulk from the pigment was also in a narrow range of 1.67 to 1.71 cm^3/g .

Sheet Stiffness. The stiffness of the four sets of sheets was remarkably close (range: 96 to 103mg).

Sheet Brightness. Since the brightness of the four SNF pigments was in a narrow range, so also was the brightness of the sheets containing the pigments in a narrow range.

Normalized Sheet Opacity. Not only the brightness of the sheets but opacity of the four different samples of SNF were virtually identical 91.2, 90.7, 90.6, and 90.9 respectively.

Scattering Coefficient of SNF. The scattering coefficient of the SNF, which is the true measure of the optical property of the pigment, was also in the close range of 2300 to 2700 cm²/g.

Conclusion:

The data indicates that the process model generated, predicted the performance of pigment in paper well. Also the process, in the lab scale, is fairly repeatable.

Task 1.2.2: Lab scale (2-gallon reactor) study (FY 2004 Q2) **a) screening of alternate raw materials**

Objective:

The objective of this task was to study the alternative silica sources for the manufacture of silicate nano-fibers with the view of ensuring adequate supply and reducing the cost of manufacturing.

Experimental:

The SNF was generally produced using fluxed calcined diatomaceous earth (DE) as the silica source. In this study we evaluated two additional silica sources:

1. Quartz
2. Sodium Silicate or Water Glass

Table 2: Process Conditions for Raw Material Screening Study

Silica Source	Batch	Product
DE	WX093	SNF
Quartz	WX094	SNF
Water Glass	WX095	SNF

DE = Diatomaceous Earth, Quartz = Crystalline Silica, Water Glass = $(\text{Na}_2\text{O})_x(\text{SiO}_2)_y$

Key Results and Discussion:

The reactions were carried out under identical process conditions for temperature, calcium/silicate molar ratio, slurry solids concentration, and impeller speed (RPM). The

resulting SNF pigment slurries were tested for calcium/silicate molar ratio and pH. The dry powders were then tested for brightness and percent water absorption.

All process conditions were identical. The only variable was the **three different sources of silica**. The three sources used were as follows:

1. Fluxed, calcined diatomaceous earth or DE (current standard)
2. Finely ground quartz
3. Liquid sodium silicate or "water glass"

Fibrous Filler Properties Using Alternate Raw Materials:

Calcium/Silicate Molar Ratio The chemical analysis of the three products was in the close range.

Brightness Sodium silicate, being the purer material than quartz or DE, gave the **highest pigment brightness**. DE gave about 1.5 points lower brightness.

Water Absorption The SNF made from quartz and sodium silicate gave 216% and 269% respectively. This value was significantly lower than the water absorption for SNF made by DE (682%). This is probably due to different molecular structures of the three silicate products.

Pigment Performance in Paper:

Hand sheets were made by standard TAPPI procedure using the three SNF pigments formed by using three different silica sources. PCC containing sheets were also made for comparison/control purposes. The sheets were conditioned (50% RH, 23°C) and calendared at constant conditions of calendaring pressure and temperature. The sheets were then tested for key paper properties. Some of the key differences were found to be as follows:

Caliper. DE gave the highest caliper. However, all three silica sources gave higher caliper than PCC.

Sheet Bulk. DE containing sheets gave highest bulk followed by sodium silicate and quartz and then PCC.

Sheet Porosity. (the higher the porosity number, more closed sheet) Sodium silicate helped improve significantly the sheet porosity over quartz, DE or PCC.

Smoothness. Here again DE gave the better sheet smoothness than quartz or sodium silicate and significantly better than PCC at equal ash of 20%.

Sheet Stiffness. DE produced the highest sheet stiffness followed by sodium silicate, quartz with PCC being the lowest.

Tensile Index. DE gave higher index than quartz or PCC but was equal to sodium silicate.

Sheet Brightness. Quartz gave the highest brightness, followed closely by sodium silicate and then DE.

Sheet Opacity. Here again quartz gave the highest opacity, DE being fairly close. However, the sodium silicate and PCC were 2.5 and 3.5 points lower than the quartz respectively.

Absorption Coefficient. The absorption coefficient of all the four materials evaluated were, within experimental error, close except for DE which was slightly higher.

Pigment Scattering Coefficient. SNF made from quartz gave significantly higher scattering coefficient than sodium silicate ($2310 \text{ cm}^2/\text{g}$), PCC ($1978 \text{ cm}^2/\text{g}$) and DE ($2883 \text{ cm}^2/\text{g}$).

Conclusion:

SNF produced from various materials gave the following results:

1. **Quartz gave the highest opacity.**
2. **DE gave an overall better product for sheet bulk, smoothness, porosity, and strength properties.**
3. **Sodium silicate made SNF produced paper with the highest brightness. However, it was lower in quality, as compared to quartz and DE. It also caused problems with a high residual pH of ~12.8.**

Task I-2.8: Comparisons of Raw Materials – Different Lime Evaluation (FY 2004 Q4)

Objective:

The purpose of this study was to compare the performance of two different sources of lime: Graymont and Mississippi Lime Company.

Experimental:

Two reactions were carried out to prepare silicate nano-fibers (SNF) using the two different lime sources and a constant silica source, namely flux, calcined silica. It can be noted that the key reaction conditions such as temperature, RPM of the impeller, calcium/silica mole ratio, and slurry solids were kept constant.

Table 3: Reaction Conditions

Description	Lime Used	DE Used
Graymont Rotary Lime (A)	Graymont Rotary Lime	WB-6
Mississippi Rotary Lime (B)	Mississippi Rotary Lime	WB-6

Key Results and Discussion

Product Properties:

Water Absorption: Mississippi Lime gave higher water absorption.

Pigment Brightness: The brightness of the product produced from Mississippi lime was lower than the SNF produced using Graymont lime.

Surface Area: The Surface area of the SNF made with Mississippi lime was lower (better) than the SNF made using Graymont lime.

Application of SNF in Paper:

Hand sheets were made using the two different SNF products produced from Graymont lime and Mississippi lime.

Discussion of Paper Performance:

Gurley Porosity (sec/100cc of air): The SNF produced from Graymont lime gave marginally higher sheet porosity (15.9 sec vs. 12.2 sec)

Sheet Smoothness: Sheets made from both SNF products exhibited similar smoothness values.

Sheet Brightness (ISO): The sheet brightness from Graymont lime was measurably higher (92.0) than the Mississippi lime (91.6). Both were only slightly better than a PCC sheet at 20% ash.

Sheet Opacity (ISO): Sheet opacity from Graymont lime was measurably higher (92.0) than Mississippi lime (91.6). Both SNF products gave ~2.5 points higher opacity than PCC.

Conclusion:

In summary, Graymont Lime (Indian Creek) was better than Mississippi Lime in the area of optical properties, which is the key attribute of silicate nano-fibers (SNF). However, Mississippi Lime gave better bulk and stiffness. Both limes were qualified for the manufacture of SNF products.

Task I-3.8: Development of New Fibrous Fillers for Low Drying Demand (SPC-LDD) (FY 2005 Q1)

Objective:

Develop a silicate macro-particle (Tech-6 low drying demand or SMP-LDD) which will have significantly lower drying energy demand than SMP and higher sheet stiffness than SNF.

Experimental:

The process conditions for the SMP-LDD are given in table 4 along with conventional SMP. Also included for comparison are the process conditions for SNF (Tech-8).

Table 4: Process conditions

Product	Pigment Properties		
	pH	Pigment Brightness (ISO)	BET Surface Area (m ² /g)

Tech-4	11.5	90.0	220
Tech-8	12.2	91.0	18.9
Tech-6	12.0	90.3	127

Key Results and Discussions:

Fibrous Filler Properties

SMP-LDD (Tech-6) was produced by increasing calcium / silica ratio. The slurry solids concentration was reduced. However, the temperature was increased. [One of the most significant effects of these changes was the reduced surface area from approximately 225 m²/g to 127 m²/g.]

Pressing and Drying Study

Hand sheets were made using the silicate products. The press solids were determined by conventional methods. The hand sheets were placed in special equipment, the Max 5000, which was used by GRI for studying the drying rate of paper. The press solids and drying rates are given as a function of surface area of Fibrous Fillers in Figure b (FY 2005, Q1).

As the surface area of SMP was from 225 m²/g the surface area of SMP-LDD was 127 m²/g, and the surface area of SNF was 40 m²/g. The press solids increased from 47% to 54%. The drying time reduced from 53 seconds to 42 seconds. In fact, Tech-6 gave even higher solids than Tech-8 (18.9m²/g.) This is illustrated in Figure 2 below.

Wet Press Solids

Conclusions:

From an energy reduction point of view, low drying demand SMP was a significant improvement.

Task I-3.7: Development of a New Fibrous Filler (Tech-6) for Reducing Drying Energy: Optimization of Tech-6 in the Lab (FY 2005 Q3)

Objective:

The objective was to optimize the new fibrous filler, Tech-6, to reduce drying energy, while improving paper stiffness.

Experimental:

Using a statistically designed experiment (D.O.E.) we produced Tech-6 in the lab. The Tech-6 from each experimental condition was tested in handsheets using standard handsheet preparation methods and paper testing. Additionally, each Tech-6 was added to a handsheet and dried using specialized drying equipment, a Comptrac Max 5000, to determine the drying demand of each Tech-6. The results were evaluated as a mathematical model correlating the independent variables with a few critical dependent variables. The independent and dependent variables for this study are given below.

Independent Variables:

1. Calcium to silica molar ratio.
2. Slurry solids concentration I.
3. The bulk temperature.

The bulk reaction time was kept constant.

Dependent Variables:

1. Surface area of Tech-6 (m^2/g).
2. Sheet opacity (normalized for basis) (ISO).
3. Sheet brightness (ISO).
4. Sheet bulk (cm^3/g).
5. Sheet porosity ($\text{sec}/100 \text{ mL air}$).
6. Sheet smoothness (Sheffield units).
7. Sheet tensile strength ($\text{N}\cdot\text{m}/\text{g}$).
8. Sheet stiffness (mg).

Key Results and Discussions:

The results of each dependent variable are discussed below. Ratio refers to the calcium to silica molar ratio. Temperature refers to the bulk reaction temperature, while solids refers to the total slurry solids concentration.

Fibrous Filler Properties:

1. Surface Area (BET)

- 1.1 Key conclusions:

- **Surface area decreased linearly with bulk temperature.**

Paper Performance:

2. Bulk
 - 2.1 Key conclusions:
 - Bulk decreased as main reaction temperature increases while leveling off.
3. Porosity
 - 3.1 Key conclusions
 - Porosity decreased with increasing temperature
 - Porosity decreased with increasing solids
 - Porosity decreased with increasing Ca/Si ratio
 -
4. Drying Time
 - 4.1 Key conclusions:
 - The minimum drying time was at a median molar ratio.
 - Drying time decreased as the bulk reaction temperature increased until the drying time levels off.
5. Smoothness
 - 5.1 Key conclusions:
 - The sheet smoothness had a significant minimum at a median ratio.
 - As bulk reaction temperature increased, the sheet smoothness improved considerably.
6. Stiffness
 - 6.1 Key conclusions:
 - As the total solids increased, the bulk temperature had an increasing influence on stiffness. At the maximum total solids, the stiffness dropped off significantly as temperature increases.
7. Tensile Index
 - 7.1 Key conclusions:
 - Tensile index generally increased with increasing bulk temperature.
 - A maximum in tensile occurred at a median ratio.
8. Sheet Brightness
 - 8.1 Key conclusions:
 - Sheet brightness increased as bulk temperature increases.
 - At the middle ratio, a maximum of sheet brightness occurred.
9. Normalized Opacity (to 74 g/m²)
 - 9.1 Key conclusions:
 - Sheet opacity increased as bulk temperature increased.
 - As solids are increased, sheet opacity decreased.

A few key observations above are repeated below to indicate what conditions may work well to reduce drying time and still maintain the qualities key to the other value propositions of SMP.

1. Drying time, and hence drying energy, was at a minimum at a middle molar ratio.
2. Drying time, and energy consumption, decreased as temperature increases until the drying time levels off.
3. The maximum sheet stiffness occurs at high total solids and low temperatures.
4. At a middle ratio, a maximum of sheet brightness occurred.
5. At a middle ratio, a maximum of sheet opacity occurred.

Conclusion:

From the standpoint of Fibrous Filler manufacturing economics, total slurry solids concentration should be increased to the maximum level technically feasible. Since the main value propositions for SMP hinge on strength properties, stiffness specifically, a lower temperature would be optimum for strength while still achieving most of the drying time savings due to increased bulk temperature. The ratio should be kept near the middle for optical properties of the sheet and drying time.

The next step in development would be to optimize SMP-LDD using alternate lower-cost raw materials.

Task I-2.3 30 Gallon reactor scale up and verification of process model (2 Gallon Reactor) (FY 2004 Q2)

Objective:

The objective of this study was to scale up and verify that the process model developed in the 2 gallon lab reactor and could be verified at 30 gallon reactor

Experimental:

Process Condition

Process condition related for this 30 gallon reactor experiment were identical as the “center point” of the 2 gallon reactor study.

Key Results and Discussions:

Pigment Properties (Table 5)

Table 5: Pigment properties for modeling and scale-up

Batch	pH	Cake Appearance	Screened Water Absorption (%)
PXPC271	10.80	Soft, Bulky	724

pH: The pigment produced in the 30 gallon reactor with the process conditions, had a PH of 10.8.

Physical Description: The dried product material was “soft and bulky”.

Water Absorption: The water absorption value of the SNF was 724%.

Performance of Pigment in Paper

The performance of the pigment in paper was evaluated in hand sheet.

Physical Properties: The other general properties of the sheet like, caliper, bulk, sheet porosity and sheet smoothness were better than PCC hand sheets.

Strength Properties: The strength properties like Gurley stiffness and tensile index were significantly better than PCC sheets.

Optical: The opacity of paper was at 1.2 points higher than the hand sheets containing PCC. All other optical properties like brightness, sealing and absorption coefficient of this sheet was better than PCC sheet.

Conclusions:

In summary, the pigment produced in 30 (thirty) gallon reactor give similar improvement in performance of paper properties as sheets in the pigments produced in 2 (two) gallon reactor under virtually identical conditions. Thus the preliminary indications were that the scale up of process from a 2 gallon reactor to a 30 gallon reactor was technically feasible. The study also confirmed the viability of process model. The next step will be to undertake a detailed “repeatability study” to confirm the trends.

Task I-2.5: Pilot-Scale (30-Gallon Reactor) Study (FY 2004 Q3)

Subtask I-2.5a: Scale-up and Verification of Lab-Scale Process Models

Objective:

The objective was to study the effect of process variables on the properties of fibrous fillers and paper made from it.

Experimental:

The process conditions from the lab-scale work (2 gallon) were tried at the pilot scale reactor. The results verified the trends seen at the lab scale. However, the performance of SNF was not as good as in the lab reactor. This was probably due to differences in reactor design and process dynamics – mass and heat transfer, etc. So a separate, new study was undertaken to model the SNF manufacturing model for the pilot scale reactor. The study, the results and the inferences are described below.

The experimental approach was to employ a statistically designed experiment (D.O.E.).

- Independent Variables:
 1. Reaction Temperature
 2. Rotational Speed of Agitator in the Reactor (RPM)
 3. Lime Slaking Methods
- Dependent Variables – Fibrous Filler:

1. Surface Area of Fillers as Measured by B.E.T. Method

- Dependent Variables – Paper Made With Fibrous Filler
 1. Sheet Normalized Opacity (ISO)
 2. Sheet Bulk Density (cc/g)
 3. Sheet Smoothness (Wire-Side Only in Sheffield Units)
 4. Sheet Stiffness

Key Results and Discussion:

Pigment Testing: The results of testing the fillers provided in the pilot reactor are given in Table 6 below.

Table 6: Pigment Properties for pilot plant optimization

Batch	Screened Water Absorption	Brightness (ISO)	BET Surface Area (m ² /g)
Pxpc 349	688	85.8	29.3
Pxpc 350	162	86.8	65.1
Pxpc 351	744	85.5	40.2
Pxpc 352	412	88.1	60.3
Pxpc 353	440	86.5	62.6
Pxpc 354	660	87.5	53.1
Pxpc 355	324	87.0	58.1
Pxpc 356	376	88.6	60.3
Pxpc 357	690	87.8	31.5
Pxpc 358	322	88.1	80.8
Pxpc 359	634	87.6	44.7

Paper Testing Handsheets were made from eleven different pigments. Sheets were tested for key paper properties like sheet opacity, bulk density, smoothness and stiffness.

Statistical Analysis and Process Model for Manufacturing SNF in the Pilot Reactor: The key inferences are discussed below.

Normalized Opacity: The main inferences are given below.

Key inferences were:

Increased temperature, lower RPM and ice slaked lime gave best results.

Surface Area of Pigment (B.E.T. in m²/g):

Significant correlations between surface area of filler and its opacifying power (sheet opacity).

Lower surface area pigment gave higher opacity.

Sheet Bulk:

Lower RPM gave higher bulk.

Sheet Smoothness:

Increased temperature and RPM decreased the smoothness value. (The lower the number, the smoother the sheet)

Sheet Stiffness :

Surprisingly none of the factors had any statistically significant influence on sheet stiffness.

Subtask 1-2.5b: Alternate Raw Material (Silica Sources) Screening at the Pilot Scale (FY 2004 Q3)

Objective:

The objective was to evaluate alternate raw materials (silica sources) in the pilot-scale (30-gallon) reactor.

Experimental:

Experiments were carried out in the pilot reactor comparing currently employed sources of silica, namely fluxed, calcined diatomaceous earth with an alternative silica source like ground quartz (Imsil A-10). The process conditions for both batches were identical and are given in Table 7.

Table 7: Process conditions for pilot plant raw material screening

Silica Source	Batch	Product
DE	Pxpc 308	SNF
Quartz	Pxpc 340	SNF

DE = Diatomaceous Earth, Quartz = Crystalline Silica

Key Properties:

Properties of Fibrous Filler (SNF):

pH: The pH of the DE batch was 11.6.

Dry Cake Appearance: The appearance of the two products was significantly different. While SNF made from DE was soft and bulky, the SNF made from quartz was hard and bulky.

Water Absorption: Here again the water absorption of DE-based product was much higher (522%) compared to SNF made from quartz (278%).

Brightness: The brightness of quartz SNF was also significantly higher (2.0 points+) than SNF made from DE.

Paper Properties

The paper handsheets were made with the two SNF products. The test results are placed in the above referred table. The key difference between DE-based SNF is referred to as **SNF-DE** and quartz-based SNF referred to as **SNF-quartz** are discussed below. The comparison was made at an equal ash level of 20%.

Sheet Bulk: SNF-DE gave higher sheet bulk.

Sheet Porosity: SNF-quartz was better in closing up the sheet (higher Gurley porosity) than SNF-DE.

Sheet Stiffness: Here again SNF-DE was 56% better than reference PCC and SNF-quartz was only 27% better than reference PCC.

Paper Brightness: In the optical properties SNF-quartz was better than SNF-DE.

Paper Opacity: Here again the SNF-quartz was marginally better than SNF-DE.

Conclusions:

Overall, SNF-quartz gave better opticals and porosity while SNF-DE gave better performance in the areas of sheet bulk and stiffness.

Task I-3.2: Pilot-Scale (30-Gallon Reactor) Study: Scale-up and Verification of Lab-Scale Process Models: Effect of Process Water and Steam Heating on SMP-LDD (FY 2005 Q4)

Objective:

During scale-up, a couple of changes in process conditions will occur. First, the water source will change from the deionized (DI) water used in the lab-scale (reverse osmosis (RO) water in the pilot-scale) to the process water in the prototype plant. Second, the lab and pilot-scale reactors are electrically heated while the prototype plant is going to be heated with direct steam injection. The effects of both of these changes were investigated in the pilot reactor.

Experimental

The 30-gallon reactor has the capacity to be heated directly with steam as well as using the electric heater. It can also use the same process water. Three conditions were tested with 2 replicate runs for each condition. The varied conditions as well as the operating conditions held constant are below. Each batch was made and tested according to TAPPI standard methods.

Constant Conditions:

Raw Materials:

- Graymont Lime's Indian Creek ½" Pebble Quick Lime
- Eagle Picher's MW-27 Diatomaceous Earth

Variable Conditions:

There were two variable process conditions.

1. Treated water (DI or RO) was replaced with mill water (process water).
2. Two heating methods were compared; namely, electrical heating and direct injection of steam to heat the reactor.

The batches produced and variable conditions used are listed below in Table 8

Table 8: Variables for reaction batches

Batch	Water	Heated
P6-538	RO	Electrical
P6-539	RO	Electrical
P6-540	RO	Direct Steam
P6-541	RO	Direct Steam
P6-542	Process	Direct Steam
P6-543	Process	Direct Steam

Results:

The handsheets from each batch were tested and the results are given below.

Fibrous Filler Properties

Pigment Properties were not tested in this experiment.

Conventional SMP-LDD. Process Conditions: Treated (RO) Water and Electrically Heated:

The SMP-LDD manufactured using RO water and electrical heaters had 20% higher bulk than market PCC while having a 200% more closed sheet (higher porosity value). The SMP-LDD sheet also had similar smoothness to a PCC sheet. The most important properties, stiffness and tensile, had very significant increases over PCC. Stiffness improved over 100% while tensile index improved over 50%. Optically the brightness dropped about 3% while normalized opacity dropped about 4%. The normalized opacity appears to have dropped more than it normally does because the 88.98 point opacity for PCC is a little higher than normal. Usually it is only 88.0-88.5 points.

Scale-Up Batches. Process Conditions: Direct Steam Injection and Mill (Process) Water:

All of the paper performance properties remained the same statistically as the conventional SMP-LDD. The only noticeable difference was in porosity for the steam heated batches. One was a 135% improvement and the other 300% compared to the ~200% improvement of all the other four batches. The average seems to be at about the same range as the other conditions but the variation seems to be greater.

General Discussion and Key Inferences:

For all technical reasons, these six different batches were statistically not different. This indicates that there is no effect on SMP-LDD of changing from DI or RO to process water or from electrical heating to direct steam injection. This means that any future work done at the pilot plant should be done with direct steam heating and using the process water available.

Conclusion:

Based on this study, we do not expect significant issues in:

- 1) Using mill water (process water), and
- 2) Using direct steam to heat the reactor.

Task I-3.18: The effect of heating time (Ramp Time) and reaction time (Soak time) at the pilot-scale (FY 2006 Q2)

Objective:

The objective was to determine the effects of varying ramp time and soak time using direct steam at the pilot scale on pigment properties and performance in paper

Experimental:

Using a statistically designed experiment we produced pilot-scale SMP-LDD (Tech-6). The Tech-6 from each experimental condition was tested in handsheets using standard handsheet preparation methods and paper testing. The results were evaluated as a mathematical model correlating the independent variables with a few critical dependent variables. The operating conditions that were held constant as well as the independent and dependent variables for this study are given below.

Constant Operating Conditions:

1. Calcium: silica molar ratio.
2. Slurry solids concentration.
3. Soak reaction temperature.

Independent Variables:

1. Ramp time from 30 to 90 minutes.
2. Soak time from 1.5 to 2.5 hours.

Dependent Variables:

Pigment Properties:

1. Surface area (BET) of SMP-LDD (Tech-6) (m^2/g).
2. Water absorption of SMP-LDD (Tech-6) (%).

Paper Performance:

3. Sheet opacity (normalized for basis) (ISO).
4. Sheet brightness (ISO).
5. Sheet caliper (mils).
6. Sheet bulk (cm^3/g).
7. Sheet porosity (sec/100 mL air).

8. Sheet smoothness (Sheffield units).
9. Sheet L&W stiffness (μNm).
10. Sheet tensile index ($\text{N}\cdot\text{m/g}$).

Key Results and Discussion:

The statistically designed experiment was analyzed. The results of each dependent variable are discussed below. “Ramp Time” refers to the amount of time taken to heat up linearly from ambient temperature up to soak temperature. “Soak Time” refers to the time the reaction is left at the soak temperature after the “Ramp Time” and before cooling begins. The results are as follows:

Pigment Properties:

1. Surface Area (BET) (m^2/g)
 - 1.1 Key conclusions:
 - **As ramp time increased, the surface area decreased from 234 to 174 m^2/g .**
 - **As soak time increased from 1.5 hours to 2.5 hours the surface continued to decrease from 198 to 155 m^2/g .**
2. Water Absorption (%)
 - 2.1 Key conclusions:
 - As soak time increased water absorption marginally decreased.

Paper Performance:

3. Normalized Opacity (to 74 g/m^2) (ISO)
 - 3.1 Key conclusions:
 - Increasing the ramp time from a minimum of 30 minutes up to a maximum of 90 minutes, marginally improved sheet opacity by ~1 point.
4. Brightness (ISO)
 - 4.1 Key conclusions:
 - A marginal increase in brightness occurred when soak time is increased.
 -
5. Caliper (mils)
 - 5.1 Key conclusions:
 - **Decrease in ramp time increased caliper.**
6. Bulk (cm^3/g)
 - 6.1 Key conclusions:
 - Marginally increased bulk results from a decrease in ramp time.

Conclusions:

The key results mentioned above are as follows:

- **As ramp time decreased, surface area and bulk increased.**
- **As soak time increased from 1.5 hours to 2.5 hours the surface continued to decrease.**
- **Stiffness can be improved marginally by decreasing the ramp time.**

In past studies, a strong correlation has been developed between surface area and drying demand. As surface area is decreased, the drying demand also decreases. As indicated above increasing soak time and to a lesser extent ramp time, surface area and drying demand can be decreased. This comes at a marginal expense of sheet bulk and stiffness, which is the driving property behind basis weight reduction in xerographic paper. That means the paper machine drying energy can be further reduced at a small expense of fiber reduction.

Task I-1.3: Commercial SMP Production (FY 2003 Q2)

Objective:

To make commercial quantities of SMP for paper machine trials.

Experimental:

In 2003, GRI only had a pilot scale reactor. GRI entered into a joint development agreement with another manufacturer who had commercial scale pressure vessels. The limitation of this manufacturer, however, was such that we could not use GRI's standard raw materials and process conditions. Thus we had to limit ourselves, for the time being, to producing only silicate macro particle (SMP). The product quality of the silicate produced in the production scale was compared to silicate produced in the industrial pilot plant. The data indicate that all key product attributes, namely, water absorption, particle size, shape and X-ray deflection, were comparable. Both products showed that there was no detectable crystalline silica. However, the brightness of the production scale was 1.4 points lower.

Table 9: Comparison of Pilot and Production SMP

	SMP Produced	
	GRI	Rented
	In Pilot Scale	In Production Scale
Water Absorption values (%)	450	520
Brightness, Blue Light (%)	90.4	89
BET Surface Area (cm²/g)	~155	254
Crystal Phase (via X-Ray Diffraction)	Partially Amorphous, Riversideite	Partially Amorphous, Tobermorite
Crystalline Silica	Below Detectable Limits	Below Detectable Limits

Task I-1.3: Lab Scale Evaluation of Commercial SMP Production (FY 2003 Q2)

Key Results and Discussion:

The handsheets were made using the silicates produced from the pilot scale and production scale plants. Analysis indicated that the sheet bulk, stiffness and brightness of the paper were nearly identical, despite use of different raw materials, process equipment, and conditions. However, the surface area, brightness, and crystal phases were different. The resulting handsheet properties were not acceptable.

Conclusions:

This indicates that the scale-up of the manufacturing of “Fibrous Filler” from the pilot scale to the production scale reactors was not successful. This is when GRI decide to build its own prototype plant.

Task I-3.15: Prototype plant construction (FY 2005 Q4)

GRI had completed the building and startup of a full-scale prototype plant to produce fibrous/engineered fillers including Tech-2 (S-PCC), Tech-4 (SMP), Tech-6 (SMP-LDD), and Tech-7 (SMF). The plant is located at Grays Harbor Paper Company (GHP) in Hoquiam, Washington.

Equipment List:

The following equipment has been purchased / leased for the startup the prototype plant.

Equipment List (Phase I):

1. Manual lime slaking system.
2. Lime screening system.
3. Manual silica slurry preparation system.
4. 5,000-gallon pressure reactor to produce Tech-2 (S-PCC), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF).
5. Product screening system.
6. Liquid CO₂ supply system to produce low cost Super-PCC.
7. Pumps and motors.

Phase I construction is estimated to cost \$1.0 million+.

These fibrous/engineered fillers will be pumped into a truck and then shipped to customers for commercial paper machine trials.

Budget and Funding:

Due to cost overruns, GRI has run into a shortage of funding. We have, therefore, cut back on buying new equipment, some automation, etc.

We are currently trying to find additional funding. There is a possibility that GRI will have a shortage of funding to operate the plant in 2006 to manufacture Fibrous Filler (SMP-LDD or Tech-6) and Super PCC long enough to fully validate the techno-economic viability of the Fibrous Filler. GRI will require additional funding for FY 2006. GRI currently has a no-cost time extension from the DOE until April 2009.

Grays Harbor Paper (GHP) Contract:

GRI received a letter of intent from GHP in May 2005. In December 2005, GHP signed an agreement with GRI for GRI to build the prototype plant at their site. The initial contract is for one year and if GRI's technology is proven to be technically feasible and economically viable, the contract can be extended for 5 years. In Phase I GRI was to supply up to 1000 tons/month of SPCC and 100 tons/month of Silicate Macro-Particles (SMP, SMP-LDD, and SMF) to GHP.

Construction and Timeline:

The construction started in the fourth quarter of 2005 and Phase I was completed in March 2006. The prototype plant produces SPCC (Tech-2), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF). All the accompany equipment for making SPCC (Tech-2), Tech-4 (SMP), Tech-6 (SMP-LDD) and Tech-7 (SMF) is installed.

The steam system and the high pressure sealing system were completed in Q2 2006.

Task I-3.20 & 21: Commercial production trials of calcium silicates for papermaking ({Tech-4} and/or SMF {Tech-7}).

See Task III-3.17 which described jointly the commercial pigment production and the associated commercial paper machine trial.

Overall Conclusions and Next Steps

GRI has been able to perform several items to forward the various silicate technologies from the R&D stage through commercial scale production. These include.

- Optimize and develop detailed predicting models for both Tech – 4 (SMP) and Tech – 8 (SNF).
- Raw Material Screening for all Tech products.
- Develop and optimize new product Tech – 6.
- Develop models for Tech – 6 performance at the lab and pilot scale.
- Design, build, and operate a 5,000 gallon commercial-scale demonstration plant to manufacture Tech – 4, Tech – 5, Tech – 6, and Tech – 7 for commercial demonstration trials at various paper mills (GHP, GP).

Scale-Up of SMP Summary

The key characteristic of the manufacturing process is that these reactions are carried out at high temperatures. The current commercial products went through several stages of development. The most challenging part was the scale-up. The various stages of scale-up (see Figure 3) were as follows:

1. 1 st stage – Lab Scale	2 gallon reactor
2. 2 nd stage – Pilot Scale	30 gallon reactor
3. 3 rd stage – Commercial Scale	5,000 gallon reactor

Figure 3: Logarithmic Scale showing size of lab, pilot, and commercial pressure reactors

Product Characteristics

These Fibrous Fillers are characterized by the following key tests:

1. Scan Electron Microscope (SEM) at high resolution (not shown),
2. X – Ray Diffraction (XRD) pattern,
3. Particle Size & Shape.

Scale – Up of Manufacturing Process

1. XRD: Figures 4 a, b, and c shows the XRD of SMP produced in lab, pilot, and commercial scale reactors respectively. The major peaks are at approximately 3.055 Å, which is characteristic of Riversideite form of calcium silicate. This clearly demonstrates that the three products that were made on these different scales are.

Figure a: Lab Scale SMP

Figure b: Pilot Scale SMP

Figure c: Commercial Scale SMP

Figure 4: XRD Diagrams showing SMP made in lab, pilot, and commercial reactors

- Particle Size: Table 10 below shows that the particle size distribution between lab scale SMP and commercial scale SMP are almost identical. D50 is a term used to describe the size mesh that 50 % of the particles will be able to pass through.

Table 10: Mean Particle Size for SMP

Scale	D50 (μm)
Laboratory	13.5

Pilot	NA
Commercial	17.2

Conclusion

As can be seen from this summary, the scale-up of SMP, and also all other Fibrous Fillers, was successful.

Task I-3.4: Optimization of Super-PCC in the Lab (FY 2005 Q1)

Objective:

The objective was to develop low cost calcium based fillers.

Experimental:

GRI's approach was to develop new filler modification:

1. Super-Precipitated Calcium Carbonate (or Tech 2) produced by GRI's patented process of pressure carbonation and a carbonate-silicate "hybrid" product (Silica coated carbonates.)

Super-PCC or Tech-2:

An optimization of the process conditions was undertaken to provide different forms of S-PCC or Tech 2.

As is well documented in the literature, conventional precipitated carbonate on a commercial scale is produced by passing flue gas (from a lime kiln) containing approximately 20% CO₂ through slaked lime slurry contained in open vessels (reactor) at atmospheric (zero) pressure. The limitation of this process is that the rate of reaction (carbonation) is slow, thus requiring large "carbonation" reactor vessels and high capital cost. GRI's patented process uses high pressure to create better product quality and to increase the reaction rate thus reducing the vessel size and capital cost. In addition to this the current study showed the GRI Super-PCC or Tech 2 also significantly reduces energy demand for drying.

Using statistically designed experiments and computerized analysis of variance (ANOVA) we developed mathematical models correlating the independent variables with a few critical dependent variables. The independent and dependent variables for this study are given below.

Independent Variables:

1. Carbonation pressure
2. Carbonation temperature.
3. Per cent CO₂

Dependent Variables:

1. Reaction (carbonation) time (minutes)
2. Surface area of S-PCC (m³/g)
3. Sheet opacity (normalized for basis.) (ISO)
4. Sheet brightness (ISO)
5. Sheet bulk (cc/g)

6. Sheet porosity (sec/100 ml air)
7. Sheet smoothness (Sheffield units)
8. Sheet tensile strength (N*M/g)
9. Sheet stiffness (mg)

Results and Conclusions:

Key Findings

Mathematical models correlating independent and dependent variables are given below. Based on these, the key findings are as follows:

1. Reaction (carbonation) time (min.):
 - 1.1 Key conclusions and mathematical model were:
 - **Reaction rate** highly correlated with **reaction pressure** – quadratic relationship.
2. S-PCC (Filler) surface area (m²/g):
 - 2.1 The key conclusions were:
 - Surface area had significant linear relationship with temperature.
 - Temperature had dominant effect over pressure and percent CO₂.
 - Pressure & percent CO₂ were covariates.

Paper Properties (Opticals):

Individual responses are as follows:

3. Normalized opacity (ISO):
 - 3.1 Conclusions
 - Strong quadratic relationship between normalized opacity and temperature. Increased temperatures gave higher opacity. However, quadratic relationship shows “diminishing” returns at temps > 40°C.
4. Brightness (ISO):
 - 4.1 Conclusions based on the above finding were:
 - Poor correlation between brightness and temperature.

Paper Properties (Physical):

The individual responses were as follows:

5. Sheet bulk (cc/g):
 - 5.1 The conclusions were:
 - Pressure and percent CO₂ had dominant effects on bulk vs. temperature
6. Porosity (sec/100 cc air):
 - 6.1 The conclusion and the mathematical models were:

- Temperature had a dominant effect on porosity. At higher reaction temperatures, porosity approaches PCC control value.
- Pressure had significant impact at all temperatures. If a higher temperature setting is selected, pressure can help compensate for loss in porosity.

7. Sheet smoothness (Sheffield units):

7.1 The conclusions and the mathematical models were:

- At higher reaction temperatures, smoothness decreased at elevated pressures. At pressure of 35 psig and 10% CO₂, smoothness marginally higher than PCC control.

Paper Properties (Strength):

The individual responses were as follows:

8. Tensile strength (N*M/g):

8.1 The conclusions correlating the process variables with tensile strength are as follows:

- At lower percent CO₂ values, pressure had a dominant effect on tensile. In general, elevated pressures increased tensile. At pressure equaling 35 psig, tensile approaches PCC control (11.1 N*m/g).
- At higher temperatures, pressure*percent CO₂ interaction present. At 35 psig and lower percent CO₂, tensile approaches PCC control.

Task I-3.6: Lab-Scale Raw Material Screening: Lime Screening for S-PCC (FY 2005 Q2)

Objective

The objective is to determine the performance in paper of S-PCC produced from various lime sources.

Experimental

Four different quick limes were tested. These sources included two grades from Mississippi Lime. One grade was a rotary kiln grade, sized less than 3/8" (labeled "Miss. Rotary Granular"). The other was a kiln process described as Peerless Granular. It was a grade sized 3/8"-5/8" (this lime labeled "Miss. 3/8" PG"). The other two grades were ~1/2" rotary kiln limes from Western Lime and Ashgrove Cement (labeled "Western" and "Ashgrove" respectively).

All four limes were slaked using the same procedure. This lime was then carbonated using the following conditions:

1. Carbonation pressure was 30 psig.
2. Original lime concentration was approximately 200g/L as CaCO₃.
3. Starting carbonation temperature was 43° C.
4. Impellor speed was 700 RPM.
5. Target carbonation reaction rate was 6.0 g/L/min.
6. Assumed carbonation efficiency was 95 %.

7. % CO₂ in the gas stream was 20 %.
8. Because the pressure had to stay at 30 psig and the CO₂ was only 20 %, the assumed CO₂ utilization was 70 %.

Each S-PCC was prepared in handsheets using standard TAPPI handsheet preparation and testing methods.

Results

The four different limes were compared to each other as PCC, using **market PCC** as the standard.

Key Findings

Optical Properties: Both Mississippi Peerless Granular and Western Lime S-PCC had the same optical properties as market PCC.

Caliper and Bulk: S-PCC made from Mississippi products had better bulk than either Ashgrove or Western Lime.

Smoothness: Ashgrove S-PCC had a significantly rougher sheet (~35% rougher than market PCC).

Porosity: An interesting side note is that all four S- PCC made from 4 different limes in this study had a significant increase in **porosity** ranging from 10 – 50% increase.

Tensile Index: All four lime sources had marginal to significant increases in tensile strength (12-25%) as compared to market PCC.

Conclusions

- **For a straight replacement of market PCC, Western Lime performed well. Western Lime has similar optical properties as SMI HO with a marginal increase in stiffness (6%), significant increase in tensile (12%) and equal properties in caliper, bulk, and smoothness.**
- **A good second choice would be Mississippi 3/8” Peerless Granular. It has similar properties to Western, but possibly marginally lower stiffness, though still statistically equal to market PCC.**
- **Ashgrove Lime gave a PCC which performed not as well as the other limes.**
- **Both Western Lime and Mississippi 3/8” Peerless Granular are technically viable lime sources for producing S-PCC. Other financial considerations would determine the overall suitability of these lime sources.**

Task I-3.4: Optimization of Super-PCC in the Pilot-Scale (FY 2005 Q3)

Objective

The objective was to scale-up the process model developed in the lab by developing a process model at the pilot scale.

Experimental

Using a statistically designed experiment we produced pilot-scale Super-PCC (SPCC or Tech-2). The SPCC from each experimental condition was tested in handsheets using standard handsheet preparation methods and paper testing. The results were evaluated as a mathematical model correlating the independent variables with a few critical dependent variables. The operating conditions that were held constant as well as the independent and dependent variables for this study are given below.

Constant Operating Conditions:

1. Carbonation pressure was 30 psig.
2. Original lime concentration was 200g/L (as CaCO₃).

Independent Variables:

- 1 Starting carbonation temperature was 25° C. to 50° C.
- 2 Percent CO₂ was 17% to 30%.

Dependent Variables:

1. Reaction (carbonation) rate (minutes to complete the reaction).
2. Surface area of S-PCC (Tech-2) (m²/g).
3. Sheet opacity (normalized for basis) (ISO).
4. Sheet brightness (ISO).
5. Sheet bulk (cm³/g).
6. Sheet porosity (sec/100 mL air).
7. Sheet smoothness (Sheffield units).
8. Sheet tensile strength (N*m/g).
9. Sheet stiffness (mg).

Results and Conclusions:

The results of each dependent variable are discussed below.

S-PCC Properties:

1. Surface Area (BET)
 - a. Key conclusions:
 - **Surface area decreased as starting temperature increased until surface area levels off at about 40-45°C and above.**

S-PCC Paper Performance:

Analysis of Paper Properties

2. Normalized Opacity (to 74 g/m²)

a. Key conclusions:

- Starting temperature is the only process condition tested that effects sheet opacity.
- **Sheet opacity has a maximum at about 40-45°C.**

3. Brightness

4.1 Key conclusions Starting temperature is the only process condition tested that effects sheet brightness.

- **Sheet brightness has a maximum at about 40-45°C.**

4. Bulk

5.1 Key conclusions:

- Starting temperature increased, bulk increased linearly.

5. Porosity

6.1 Key conclusions:

- A linear relationship between starting temperature and porosity existed. Porosity values decreased as starting temperature increased.

Conclusions

As starting reaction temperature was increased, the surface area decreases reaching a minimum at 40-45°C. At this temperature, we get maximum sheet brightness and opacity. Percent CO₂ had minimal effects on pigment properties and paper performance. Thus, starting temperature at 30 psig pressure yielded the optimum product.

Task I-3.8: Scale-up Preparation for S-PCC (Tech-2) (FY 2005 Q2)

The S-PCC scale-up **from a 2 gallon lab reactor to the 30 gallon pilot reactor** was completed. As indicated in Task I-3.4, several batches of S-PCC were produced. Over 150 batches of S-PCC were also produced at the pilot-scale for a commercial paper machine trial at Grays Harbor. This paper machine trial is mentioned in Task III-3.4 (FY 2005, Q2). The scale-up include the following additions to the pilot facilities:

- Engineering a liquid CO₂ supply system.
- Modifying the reactor to accept CO₂ gas.

Conclusions

GRI has made several improvements to its S-PCC product using the grant from the DOE. These improvements include:

- **Design Modeling for S-PCC**
- **Raw Material Optimization**
- **Scale-Up to Pilot and Commercial Scale Production.**

TASK II: -Lawrence Livermore National Laboratories:

To study and elucidate the mechanism of Silicate Nano-Fiber and Silicate Macro-Particle formation.

II-1.1 Lab Preparation of GRI's Standard Silicate Nano-Fibers

Objective

To elucidate the mechanism of Fibrous Filler formation from lime and silica (DE) employing the following approaches:

- To duplicate GRI's process to prepare Silicate Nano-Fibers (foshagite, xonotlite) in LLNL's lab using their equipment.
- To analyze different solid phases during the process
- To analyze the composition fluid phase throughout the reaction

Experimental

PROGRESS REPORT #2 LLNL/FIBROUS FILLERS PROJECT

Research Associates: Sarah Roberts, Brian Ridolfi, Kevin Knauss, and Brian Viani

INTRODUCTION

Since Progress Report #1 we have completed five more synthesis runs in an attempt to produce the baseline product identified as Tech 8 GRI. During the reporting period, Sarah Roberts met with GRI project members to present previous results and to gain advice for implementing the GRI baseline protocol at LLNL. The rocking autoclave used for the first LLNL run (Roberts et al., 2003) was used for the second synthesis run (FF 2). However, because of the difficulty in matching the temperature ramp rate and the mixing requirement for the GRI baseline protocol using the rocking autoclave, we decided to use a stirred batch reactor (described below) for subsequent synthesis runs. We believe the batch reactor affords a better opportunity to match the GRI baseline protocol. Because of operational shakeout problems with the batch reactor and lack of a cooling feature, there are still differences between the GRI baseline protocol and the reaction conditions used for LLNL runs 3 to 6. We believe we have solved the equipment problems and plan to adapt our batch reactor to provide for direct cooling to be able to match the cool-down rate in the GRI protocol. Characterization of solid products and fluid and solid samples collected during the runs are presented for runs 4 to 6 (results from FF 3 are not reported because the stirring apparatus failed). Although the protocols used do not yet match the GRI baseline, based on surface area analysis of the products, two of the runs (FF 4 and FF 5) yielded material that may have acceptable properties for its projected use.

EXPERIMENTAL

The different LLNL experimental synthesis runs are indicated as FF 2, FF 3, FF 4 etc. Fluid and solid samples collected during the runs are indicated as FF 4-1, FF 4-2 etc.

Materials – The starting materials we used were Dicalite WB-6 Diatomite, and pebble Mississippi Lime. Pebble CaO was slaked and available CaO determined as previously noted (Roberts et al. 2003). Because apparently significant amounts of calcite were detected via XRD in intermediate run samples and in final products, the pebble lime reactant and slaked lime slurry were analyzed for calcite. XRD analysis of the pebble lime indicated only lime with a minor amount of portlandite (Figure 1). Chemical analysis of the slaked lime slurry (inorganic carbon analysis) indicated approximately 2.7% calcite. Calcite is also evident in the XRD scan of solids separated from the slurry by centrifugation and dried at 50 °C under N₂ to prevent formation of additional calcite via absorption of atmospheric CO₂ during drying. We believe the bulk of the CO₂ was absorbed during the sieving process following the slaking of the pebble lime. BET analysis of the slaked lime (dried under N₂) yielded a surface area of 19.0 m²/g. Because some CO₂ absorption and calcite formation would be expected for commercial scale syntheses, we did not attempt to prepare a carbonate-free slaked lime slurry.

Key Results

LLNL reported that although the protocol used in the lab did not yet match the GRI baseline, based on surface area analysis of the product, two of their latest runs (FF4 and FF5) yielded material that may have acceptable properties for its projected use. However, their initial results provided some insight into the mechanism of formation of Fibrous Fillers. We then stopped further work on this task.

Key Findings (Run FF4-FF6)

- Found **Scawtite**, a calcium silicate carbonate hydrate with a calcium/silica ratio of 1:1.17.
- Also reported large amounts of **calcite**.
- In the latest run some trace amount of **Foshagite** was detected.
- Intermediate solid phase analysis significant. Results showed that the surface area of the intermediary phase goes up to 157 m²/g and then it falls to ~20-30 m²/g as the reaction nears completion. Also identified **Trabzonite** as an intermediary product.
- In the fluid phase the calcium concentration rose rapidly to 400-500 ppm and then dropped to 100 ppm. The dissolved silica in all the experimental runs (FF4-FF6) never rose above 4.0 ppm, which shows that Cristobalite, though present in some samples, FF4 and FF5, is not controlling Si anywhere near equilibrium values (~350 ppm).
- In short, LLNL has made significant progress. They need to still produce on a consistent basis, and to duplicate GRI's process and "Fibrous Fillers" (Foshagite).

We have since canceled the contract with LLNL.

We have retained, as an advisor, an expert on silicate chemistry, Dr. Della Roy of Pennsylvania State University.

TASK III – GRI & Paper Companies:

Development of Ultra-High Ash Paper (Up to 50% Calcium and Silica Based Filler).

Filler Optimization (FY 2003 Q2)

Objective

Optimization of calcium carbonate + silicate macro particle (Tech 4) at different ash levels.

Experimental

The experiment was carried out according to a statistical design-of-experiments (DOE). The handsheets were tested for key paper properties. The resulting data was statistically analyzed and mathematical models were developed correlating the Tech 4 to PCC ratio, and total % ash with key paper properties.

Conclusions

The data further confirms that calcium silicate product improves sheet bulk, caliper, stiffness and smoothness, simultaneously.

Basis Weight Reduction and Fiber substitution (FY 2003 Q2)

Objective

To produce a lower basis weight sheet (19#/3300ft²) having key paper properties equal or better than a higher basis weight sheet (20#/3300ft²) at equal or higher filler levels.

Experimental

Handsheets were made using market PCC at 20 # while handsheets containing silicate macro particles were made at 20 and 19 #. The handsheets were calendared to equal smoothness and conditioned.

Key Results

It was showed that the caliper of a 19# sheet containing silicate macro particle (SMP) was equal or better than a 20#/3300ft² sheet containing an equal amount of PCC ash. The stiffness of the lower basis weight sheet was equal to, or better than, the higher basis weight sheet (20#/3300ft²) containing PCC only.

Conclusions

This study indicated that a lower basis weight sheet can replace a higher basis weight sheet at equal or even higher ash levels. This confirms that GRI's silicate macro particle (SMP) can significantly improve sheet, bulk and stiffness. All figures can be found in FY 2003, Q2's report.

The potential cost savings ~ \$20 to \$30 per ton.

Task III-2.1 To study the effect of high "Fibrous Filler" (25%-50%) content on paper properties and paper processes (combination of silicate nano-fibers and silicate macro-particles) (FY 2004 Q1).

Objective

To optimize the combination of fibrous fillers (SNF in Figure 2 and SMP in Figure 3) and PCC (Figure 4) to manufacture ultra high ash papers (40%+).

Experimental

Materials:

The materials used in this study, along with their key characteristics are given in Table 12. The SEP pictures of all three products are given in Figures 7 and 8.

Table 11: Pigment properties

Pigment	Mean Particle Size (micron)	XRD Analysis	Surface Area (m ² /g)
SMP	~15	Riversideite	200.0
SNF	~20	Foshagite	20.0
PCC	~2.0	Calcite	4.0

Design of Experiment:

A statistical design of experiment (D.O.E.) was adopted to study the effect of “mixtures” of fibrous fillers, SNF and SMP, and PCC on paper properties. A geometrical representation of the “mixture” design is given in Figure 5.

Figure 5: 2-D diagram of data points at 3 ash levels

In addition to the above, the effect of ash level was also studied. The geometry of the complete design is further represented in Figure 6.

Figure 6: 3-D diagram of data points

The hand sheets were made according to the experimental conditions described above. The sheets were conditioned, calendared and tested for the following key paper properties.

- Sheet Bulk
- Smoothness
- Porosity
- Stiffness
- Brightness
- Normalized Opacity

Key Results and Discussion:

Statistical Analysis

The results of the testing were analyzed using Minitab, a statistical analysis software tool. An example of the three-dimensional plots is given below in Figure 11.

Key Findings:

Sheet Bulk. The sheet bulk for the conventional filler PCC decreased with increasing ash level. However, fibrous fillers increased the bulk with increasing ash level, particularly using silicate macro-particles. The 3-D surface plots also confirm the same trend.

Sheet Smoothness. It was interesting to note that sheet smoothness improved for silicate nano-fibers. The 3-D plots further show the effect of mixtures of SMP, SNF and PCC at 15, 30 and 45% ash levels.

Sheet Porosity (Gurley). The most significant result was that sheet porosity improved 7-fold (higher number is better) as silicate nano-fiber addition level increased from 15 to 45%. At 30% and 45% addition levels there was a “curvature” or synergistic effect among the three pigments.

Sheet Stiffness. Here again the sheet stiffness of PCC-containing sheets reduced considerably as the ash level was raised from 15 to 45%. The SMP, on the other hand, increased the stiffness with increasing ash level. There is also a significant synergistic effect between the three pigments (see Figure 7).

Figure 7: 3-D plot of stiffness at 45 % ash

Sheet Brightness. Silicate nano-fibers gave higher brightness than PCC at all ash levels. The overall sheet brightness increased as nano-fibers levels were increased in the 3-component pigment mixtures.

Sheet Opacity. Silicate nano-fibers gave 2-3 points higher opacity than PCC. There was also a significant “curvature” effect among SNF, SMP, and PCC.

In summary, it would be possible to make an ultra-high ash sheet without losing bulk and sheet stiffness using a combination of silicate macro-particles and silicate nano-fibers.

Silicate Nano-Fibers. Silicate nano-fibers can be best utilized for improving sheet optical properties, smoothness and sheet porosity.

Silicate Macro-Particles. Silicate macro-particles, on the other hand, are best suited for improving sheet bulk and stiffness.

Conclusions

- A combination of silicate nano-fibers (SNF), silicate macro-particles (SMP) and S-PCC produced ultra-high ash papers. The 30% and 45% SMP sheets had higher stiffness than the 15% PCC sheets.
- A combination of the three pigments at 30 % ash had higher stiffness than 15 % PCC.
- At 45 % ash, consisting of a combination of these pigments, was statistically equal to 15 % PCC.

Thus, we clearly met the objective of the program of producing ultra-high ash paper with equal or better paper performance.

Task III-3.1: Study the Effects of Pressing on Drying Energy (FY 2005 Q1)

Objective:

To study the water removal by pressing and drying.

Experimental:

Materials following a pigment were used in the study.

1. Silicate Nano Fibers (SNF or Tech-8)
2. Silicate Macro Particles (SMP or Tech-4)
3. New / modified Silicate Macro Particles with Low Drying Demand (SMP-LDD or Tech-6)
4. Super Precipitated Calcium Carbonate (Super-PCC)
5. Conventional Precipitated Calcium Carbonate

Hand sheets were made using the above mentioned fillers. Hand sheets were passed through the wet press three times. The press solids were determined after each pass. Hand sheets were dried in a special drying balance which recorded time taken to dry the sheet to equal moisture level (~50 %.) The hand sheets were tested by standardized TAPPI methods.

Key Results

Key Findings:

- S-PCC gave ~ 59% solids off the pressing section as compared to 49% for conventional PCC – an increase of 10% press solids.

Press Solids

- New and modified SMP-LDD gave 50.5% solids as compared to 43.34% solids off the press section by SMP – an improvement of 7.0% solids.
- SMP-LDD also gave equal press solids of 53 % as PCC after 3 passes and equal drying time of 41 minutes.
- The details of how well each pigment responded to pressing can be seen in Figure 8.

Wet Press Solids

Figure 8: Graph showing solids at each press

Drying Time:

GRI's S-PCC is the easiest to dry among all the filler with drying time of only 38 minutes as compared to conventional PCC at 45 minutes.

Drying Energy:

Fig. 9 demonstrates that if the press solids are increased by 10% (from 40% to 50%) the steam required to dry a ton of paper goes down from 3500 lb to 2100 lb which is a 40% reduction in energy consumption.

Figure 9: Diagram showing energy usage to dry paper at various press solids

Conclusion:

The pressing study demonstrated that we successfully developed a low drying demand (SMP-LDD) comparable to PCC. Also GRI's S-PCC gives significantly higher solids than market PCC.

Paper Performance:

Key Findings

1. SNF gave the highest opticals and good press solids and drying time (lower drying energy)
2. SMP gave the highest sheet bulk and stiffness
3. SMP-LDD gave the highest press solids and drying rate (lower energy)
4. S-PCC gave the highest press solids of any products tested

Conclusions

By comparing various GRI pigments, we can optimize the energy uses and paper properties.

Task I-3.16: Commercial production trials of nano-carbonates (SPCC or Tech-2) (FY 2006 Q1).

Objective:

The objectives were:

1. To scale-up the production of S-PCC in the 5,000 gallon reactor and
2. evaluate it's performance on commercial paper machines

Experimental:

Nano-carbonates (SPCC or Tech-2) were produced in our 5,000-gallon prototype reactor. Several of these batches were produced for each of the two commercial paper machine trials at Grays Harbor Paper. The conditions for a typical batch are displayed below in Table 12. Each commercial paper machine trial was conducted by removing the market PCC and replacing it with the SPCC. Each condition was tested by testing the end of each reel of paper produced, then averaged for each condition.

Table 12: Reaction Conditions for commercial batch of S-PCC

Conditions	Typical SPCC Batch (GHP2-4)
Concentration (g/L)	290
CO ₂ Concentration (%)	100% (Liquid CO ₂)
Reaction Time (min)	112 (CO ₂ limited)
Reaction Rate (g/L/min)	2.6

Key Results and Discussion:

Both commercial paper machines during both trials indicated approximately the same results. For the sake of explanation, the results on one paper machine during the second trial are discussed. The performance of SPCC compared to market PCC is given below for each key paper property:

Key Findings

Gurley Porosity (s/100cc). Porosity of SPCC-containing sheets was significantly better than market-PCC sheets with an 11.5% improvement.

Sizing (HST) (s). A 6.8% improvement in sizing occurred due to the replacement of market PCC with SPCC in the paper produced.

Sheet Brightness. Sheet brightness was marginally improved with only a 0.3% improvement using SPCC versus market PCC.

Burst Index. Burst index was improved by 10% when SPCC replaced market PCC in the sheet.

Drying Energy Savings. The steam pressure of the drying sections during pretrial period where PCC-containing paper was produced and the trial period where SPCC-containing paper was manufactured were compared (See Table 13). The first dryer section had a reduction in steam pressure of 8.7%, the top dryer section post-size press had a reduction of 4.6%, and the bottom section post-size press had a reduction of 5.2%. Although Grays Harbor Paper doesn't have dryer section flowmeters, they have developed a steam pressure reduction versus dryer savings correlation. The overall analysis indicates that a 1.5-2.0% overall drying savings can be achieved by replacing market PCC with nano-carbonates (SPCC or Tech-2). A graphical representation of the data is given in Figure 10.

Table 13: Steam pressure during S-PCC trial

Time Period	PM #1 Main	PM #1 After Size Top	PM #1 After Size Btm
Pre-Trial	33.4	32.6	29.0
Trial	30.5	31.1	27.5
% Change	8.7%	4.6%	5.2%

Figure 10: Diagram of Steam pressures during S-PCC trial

Conclusions:

The key highlights are:

Comparison of S-PCC with Market PCC

- 1.5-2.0% lower in drying demand,
- 10% higher in burst strength
- 6% smoother,
- 7% more sizing (water resistance) and
- 11% more closed.
- The remaining key properties had no statistical differences when SPCC was added instead of market PCC. These properties included sheet caliper, sheet bulk, sheet brightness, sheet opacity, stiffness and tensile.

These points indicate that SPCC can not only perform as well as market PCC, but can also reduce energy consumption and improve smoothness, porosity, sizing, and burst strength.

Task III-3.15: Commercial paper machine production trial using commercially produced silicate “Fibrous Filler” (SMP {Tech-4} and/or SMF {Tech-7}) at Grays Harbor Paper Co., Hoquiam WA (FY 2007 Q2).

Objective:

The objective of this trial was to reduce basis weight while maintaining other sheet properties using GRI's Silicate Nano-Fibers, including its newest product Tech-7.

Experimental:

The main focus of this trial was to **reduce the basis weight of premium xerocopy paper** while maintaining stiffness. The decision was based on the encouraging results seen in trial # 8. This was done by removing 8% of the PCC and replacing it with a mixture of SMF and SMP. Using the prototype reactor located at the Grays Harbor Paper mill site, commercial quantities of SMF (Tech-7) and SMP (Tech-4) were produced. The SMF and SMP produced were then utilized on one of the paper machines at Grays Harbor Paper to qualify the performance of the combination of SMF and SMP. This trial focused on GHP's premium xerocopy paper. Several batches of SMF and SMP were produced in our 5,000-gallon prototype reactor. These batches were produced for a machine trial at Grays Harbor Paper.

The commercial paper machine trial was conducted by replacing 5 % PCC with the SMF/SMP combination while reducing the basis weight from 20 # to 18.5 #. Each condition was tested by testing the paper properties and performance on a copy machine of each reel of paper produced.

Key Results and Discussion:

The Surface area of the combination filler was 188.1 m²/g. The average BET of the SMP was about 300 m² / g and the SMF was about 80 m²/g. The mean particle size for both was between 12 and 16 microns.

The paper samples taken from each reel were tested with TAPPI standard conditions

Operating Conditions

With the addition of SMF/SMP, the paper machine experienced no change in its **machine speed** and almost no additional drying energy was required. There was almost no change to the wet-end chemistry outside of more surface sizing.

Physical Properties

The sheet bulk for the calcium silicate containing reels of the trial was significantly higher than PCC containing paper (control). For the main portion of the trial the calendaring of the paper was held back and both the sheet's caliper and bulk were increased.

The porosity of the calcium silicate containing sheets increased significantly during the trial (74-124%) compared to the PCC containing control.

Strength Properties

The stiffness in the machine direction was lower for the trial (-17%). In the cross direction, the stiffness of the 19.0 # reel was slightly lower than the control (-2.5%), but still within the range of sellable paper.

Optical Properties

The brightness of the calcium silicate containing sheets was better than the PCC containing control (1.5%). The opacity of the reels was more than the control (+2.4%)

Conclusions:

The key highlights are:

GRI's SMF/SMP-containing paper at equal ash compared to market PCC sheets were:

- Reduced Basis Weight by 7%
- Slight loss in CD stiffness.
- Much higher porosity (closed sheet).
- Slightly higher smoothness.
- Equal productivity on the paper machine.
- Slightly more steam drying demand.
- Improved optics.

GRI's SMF/SMP was able to reduce the basis weight by 1.0#, now the focus needs to be on repeating the trial from FY06 Q4 while reducing the wet-end costs for improved economics.

Task III-3.11b: Commercial paper machine production using commercially produced silicate "Fibrous Filler" (SMP {Tech-4} and/or SMF {Tech-7}) (FY 20066, Q3).

Objective:

Using the prototype reactor located at the Grays Harbor Paper mill site, commercial quantities of SMP (Tech-4) and SMF (Tech-7) were produced. The SMP and SMF produced was then utilized on the one of the paper machines at Grays Harbor Paper to qualify SMP and SMF performance. This trial focused on GHP's offset paper.

Approach:

The main focus was improving the stiffness of the offset paper while maintaining or enhancing the improvements from the last trial.

Silicate Macro-Fibers (SMF or Tech-7) were utilized with a smaller portion of Silicate Macro-Particles (Tech-4) to aid stiffness while maintaining dryer demand and optical properties. The SMP and SMF were produced in a 15% SMP and 85% SMF ratio. This was produced in our 5,000-gallon prototype reactor. These batches were produced for a commercial paper machine trial at Grays Harbor Paper.

During this trial a small portion of the SMP/ SMF combination was placed on the sheet at the size press to see if this gave an improvement in stiffness. At the same time, a charge neutralizing chemical was added to the SMP/ SMF combination as it entered the wet end of the paper machine.

The commercial paper machine trial was conducted by removing a portion of the market PCC and adding the SMP/ SMF combination. (In some cases, the overall filler content was increased.) Each condition was tested by testing the end of each reel of paper produced.

Results:

The paper samples taken from each reel were tested with TAPPI standard conditions.

Wet End/ Running Conditions

First, the pH was successfully controlled the headbox pH to a range from 8.0-8.5, which was well within the range that the representatives from the retention chemical company felt would maintain the retention mechanism. We also improvements in the first-pass retention of the Fibrous Fillers.

Physical Properties

Overall sheet bulk was not significantly changed (2%) from the PCC control sheets. This meant that at the same basis weight as the control the caliper was increased 4%.

Due to the Fibrous nature of SMP and SMF, the sheets with SMP/ SMF were much more closed sheets (less porous) (90% better) than the PCC-containing control sheets.

The SMP and SMF filled sheets gave much smoother (13-15% smoother) sheets than the control sheets.

Strength Properties

The stiffness of the reels with SMP/ SMF combination was slightly higher in the machine direction (1%), but lower in the cross direction (-6%). When the SMP/ SMF combination was also added as a coating on the sheet the reverse trend appeared. The machine direction stiffness dropped to 7% worse than the PCC control sheets, but the cross direction stiffness increased by 1% over the PCC control sheets.

The tensile index was 18% lower in both directions for the SMP/ SMF containing sheet as compared to the PCC-containing control sheets.

Optical Properties

In the Fibrous Filler containing sheets the brightness of the SMP/ SMF was almost equal (+.8 points) than the brightness for the PCC-containing sheets. The opacity was much higher (+3.2 points).

Conclusions and Discussion:

The key highlights are:

- The SMP and SMF filled sheets gave much smoother (13-15% smoother) sheets than the control sheets at equal calendaring condition.
- The stiffness of the SMP/ SMF containing sheet was higher than the control by 1% MD, but lower by 6% CD. The addition of SMP and SMF to the size press of the paper machine reversed this result. The CD stiffness was improved by 1% over the control, while the MD stiffness was lowered to 7% under the control.
- The optical properties of the sheet containing SMP and SMF were improved.

The stiffness was not improved as much as was hoped for. However, it was observed that it is possible to target a specific direction on the paper machine for improvement. The charge-neutralization additive did appear to help.

Task III-3.16: Commercial paper machine production trial using commercially produced silicate “Fibrous Filler” (SMP {Tech-4} and/or SMF {Tech-7}) at Georgia – Pacific Co., at Camas, WA (FY 2007 Q3).

Objective:

Using the prototype reactor located at the Grays Harbor Paper mill site, commercial quantities of SMF (Tech-7) and SMP (Tech-4) were produced. The SMF and SMP produced were then utilized on one of the paper machines at Georgia - Pacific to qualify the performance of the combination of SMF and SMP. This trial focused on an integrated mill's xerocopy paper.

Experimental:

The main focus of this trial was to **reduce the basis weight of xerocopy paper** while maintaining stiffness. The decision was based on the statistical analysis done in the last quarter. Several batches of SMF and SMP were produced in our 5,000-gallon prototype reactor. These batches were produced for a machine trial at –an integrated mill. The commercial paper machine trial was conducted by replacing 8 % PCC with the SMF/SMP combination while reducing the basis weight from 47.5 # to 45 #. Each condition was tested by testing the paper properties and performance on a copy machine of each reel of paper produced. After 60 tons of reduced basis weight paper was produced, the paper moisture and ash will both be increased to see any improvements in economics without sacrificing strength.

Key Results and Discussion:

The average BET of the pigment mixture was 183 m²/g. The average BET of the SMF was 87 m²/g. The average BET of the SMP was 300 m²/g.

The paper samples taken from each reel were tested with TAPPI standard conditions.

Wet-End Properties:

The holes and defects seen in earlier trials had been overcome in this trial.

The strategy of using cationic retention aid worked because the first pass ash retention remained stable at 55 %.

The pH of the system was stabilized to 8.0 by a small flow (0.5 gpm) of phosphoric acid.

There were no reported changes in machine speed or dryer demand.

Physical Properties:

The basis weight of the sheet was lowered by 5% over the course of this trial. The caliper still showed improvement (+2.2 %). The smoothness rose slightly (i.e. became rougher) (+ 5 %). The porosity increased as seen in previous trials (+ 11.8 %). However, it was noted that the formation (a measurement of the variability in the sheet density) improved significantly (+31.5 %).

Strength Properties:

The CD Stiffness was the main property to be maintained in this trial. This succeeded. The CD stiffness was unchanged (0.0 %). At the same time the MD stiffness was improved (+ 10.1 %). The MD tensile also improved (10.7 %), but the CD tensile was slightly worse (-1.1 %).

Optical Properties:

Both Brightness and Opacity dropped in this trial (0.6 and 1.6 points respectively).

Conclusions:

Overall, this trial showed a great deal of promise. The key improvements include:

- **Maintaining CD Stiffness**
- **Reduce Basis Weight**
- **Improve Bulk**
- **Maintain production rate**
- **Improved Formation**
- **Stable first pass ash retention**

The main issues that arose from this trial was the reduction in the optical properties.

TASK IV - Western Michigan University:

Optimization of surface treatment formulations.

IV-1.1. Optimization of surface treatment formulations containing Silicate Nano-Fibers ("Fibrous Fillers").

Objectives

The objective of this phase was to study:

- a) The influence of Silicate Nano-Fiber concentration on the rheology of starch and polyvinyl alcohol solutions,

- b) To determine optimum Silicate Nano-Fiber to binder ratio,
- c) To study the mechanism of Silicate Nano-Fiber bonding to substrate and dried coating layer,
- d) To compare Silicate Nano-Fibers with Optisil and fumed silica using polyvinyl alcohol as binder.

Experimental

Materials

- GRI's Silicate Nano-Fibers (SNF a.k.a. TiSil or Tech-8)
- Silica gel (Sylojet, W.R. Grace Co.)
- Precipitated calcium silicate (Optisil, Huber Co.)
- Fumed silica
- Starch (cationic potato)
- Polyvinyl alcohol (PVOH 418)

Equipment

- Draw downs on Mylar using various Mayer rods

Key Measure / Tests

Test

Dry coating structure particle size

Brightness

Opacity

Gloss

Dusting tendency of coatings

Printing

Ink densities

Rheology

Dynamic

Equipment

B.E.T. analyzer (TriStar)

TB-1-C

TB-1-C

BYK multi-angle glossmeter

Black cloth

Stylus Pro 900 PIE 20 printer (Epson)

X-Rite 408 reflectance densitometer

Brookfield RVT Viscometer and Rheometrics

Stress Rheometer

The three different microfiber to binder ratios, viz 80/20, 70/30 and 60/40, were used. Coating was applied on a 62 gsm coated base sheet with a target coat weight of ~10 gsm on each side. The samples were then calendared. Both uncalendered and calendared sample were tested for brightness, opacity and gloss, and 'dusting' tendency. Similar treatment was given to a silica gel coated sheet as a control for comparison. Also, a commercial paper, Hammermill JetPrint UltraMatte 26 pound was also printed for comparison.

Results

The initial screening study indicated that SNF and PVOH 418 at 70% pigment and 30% binder gave optimum coating properties for ink jet paper. SNF: PVOH 418, 70:30 formulation coating was compared with Optisil:PVOH 418, 70:30 and fumed silica:PVOH 418, 7:1. The results are given in Table 65.

Key Findings and Inferences

- Coating Brightness of SNF (Fig. 11) was slightly lower than Optisil and fumed silica and significantly higher than commercial ink jet paper.
- Coating Opacity (Fig. 12). Coating opacity of GRI's Silicate Nano-Fiber, PVOH 418 formulation was significantly higher than Optisil but lower than fumed silica and commercial ink jet paper.

- Coating Gloss (75°) (Fig. 13). Silicate Nano-Fiber sheets had better sheet gloss than commercial ink jet paper and sheets containing Optisil. However, fumed silica gave the highest sheet gloss.
- Black Print Density. Commercial ink jet paper had the highest print densities as compared to the three lab formulations. It appears that commercial product had some additional additives like dye fixation, which were not included in the lab formulations.
- Black Print Gloss. Silicate Nano-Fiber gave higher print gloss than commercial paper but much lower print gloss than both Optisil and fumed silica formulations.

Figure 11: Coating Brightness

Figure 12: Coating Opacity

Figure 13: Coating Gloss

The WMU data also showed that the SNF formulation had much higher absorptivity due to larger pore volume and lower surface area. This may be the reason that the black ink densities and printed gloss of SNF sheets were lower than Optisil and fumed silica.

Conclusion

GRI's SNF gave excellent optical properties and gloss, and Silicate Nano-Fibers are more suited as a pigment for matte finish, not for high gloss finish.

The various tables and figures can be found in FY 2003, Q4.

After the initial work, the work had been completed.

Overall Conclusions

GRI has been able to demonstrate the techno – economic feasibility and economic advantages of using its various products in both handsheets as well as in commercial paper mills. GRI has also been able to develop sophisticated models that demonstrate the effect of combinations of GRI's fillers at multiple filler levels. GRI has also been able to develop, optimize, and successfully scale-up new products for use in commercial paper mills.

Economic Analysis and Value Propositions

The value proposition or benefits from Synthetic Nano Materials are derived due their unique product attributes. The following are some examples of how the properties of the Fibrous Fillers, compared to pulp fibers and other materials, causes the changes in paper properties and their end-use performance.

1. Caliper	↑ Up
2. Bulk	↑ Up
3. Stiffness	↑ Up
4. Smoothness	↓ Down
5. Porosity	↑ Up
6. Brightness	↑ Up
7. Opacity	↑ Up
8. Sheet Moisture	↑ Up
9. Fiber Requirements	↓ Down
10. Energy Consumption	↓ Down

In general terms, these SNM can partially replace wood pulp fibers, chemicals, and more expensive materials like Titanium Dioxide (TiO₂). In the following section, we will review the effect of these unique properties on the economics, looking at both cost reduction and higher revenues.

Reduce Paper Weight per unit area → Fiber Elimination

By adding SNF into paper, the basis weight (mass per unit area) can be reduced by 10 % – 15 % (higher bulk). This is because adding SNF into paper increases the caliper by 10 – 15 % and consequently the stiffness of the paper has been increased. Thus the basis weight of the paper can be reduced by 5 – 10 % while still maintaining equal stiffness (a key paper property for P, W, X grades). The value of each 0.1 # reduction in basis weight is given below in Figure 14 (for an integrated paper mill) as well as Figure 15 (for a non-integrated paper mill).

- Integrated Paper Mills

Figure 14: Costs savings as basis weight is reduced for P, W, X grades at an integrated paper mill

The potential savings by reducing the basis weight 5 – 10 % for an integrated paper mill is in the range of \$ 5 / ton to \$ 23 / ton. Refer to Figure 14 to see that the cost savings are positive below a basis weight of 19.2 # / 1300 ft².

- Non – Integrated Paper Mills

Figure 15: Cost savings as basis weight is reduced for P, W, X grades at a non-integrated paper mill

For a non-integrated paper mill which has to buy market pulp at about \$ 600 / ton, the savings the mill could possibly obtain is in the range of \$ 16 / ton to \$ 47 / ton. Refer to Figure 15 to see that the cost savings are positive below a basis weight of 19.5 # / 1300 ft².

Increase Filler Level → Fiber Substitution

The Fibrous Fillers has unique length to diameter ratios, unlike currently used commercial fillers. This allows paper mills to further replace wood fibers in paper with fillers from about 15 % to 30 % or more, a 100 % increase in the filler level. The savings shown in Figures 16 and 17 shows the savings for an integrated and non – integrated paper mill respectively.

- Integrated Paper Mills

Figure 16: Cost savings by increasing ash levels in P, W, X grades at an integrated paper mill

For an integrated mill, the cost savings by increasing ash level can range from \$ 3 / ton to \$ 17 / ton. Refer to Figure 16 to see that the cost savings are positive above an ash level of 17.6 % ash.

- Non – Integrated Paper Mills

Figure 17: Cost savings by increasing ash level in P, W, X grades at a non-integrated paper mill

For a non – integrated paper mill, the effect of increasing the ash level from 15 % to 30 % can be much higher, in the range of \$ 19 / ton to \$ 56 / ton. Note that in Figure 17, the cost savings in immediately positive.

Increase Moisture Content → Fiber Substitution

Fibrous Fillers absorb moisture. The water absorption of SNF is between 400 % and 1000 %. Thus, in the paper sheet, the equilibrium moisture content (the amount of water the paper will hold if left alone for a long time (2 + hours)) will be higher. This has two main benefits for the paper mills

1. **Cost Savings:** Paper mills are shipping more water (which is virtually free) instead of pulp and other raw materials (which cost money) in every sheet of paper. This means that they are making money on selling more water and not consuming raw materials.
2. **Less Drying Energy:** Paper mills have to run their paper through a series of dryers to bring the paper close to it's equilibrium moisture content during the papermaking process in order to keep the sheet from having defects during the process where rolls of paper are cut into letter sized paper, legal sized paper, and other paper sizes that are then sold to consumers. With the equilibrium moisture level higher, the paper mills do not have to

use as much energy to get the same amount of paper to its final moisture level. This constitutes an energy savings for the paper mill.

Figures 18 and 19 shows the cost savings that an integrated and non – integrated paper mill can see respectively.

- Integrated Paper Mills

Figure 18: Cost savings for inceasing moisture content in P, W, X grades at an integraed paper mill

In an integrated paper mill, the increase in moisture form 4.5 % to 5.3 % can reduce the cost of production from \$ 2.5 / ton to \$ 5.7 / ton. Note that in Figure 18, the cost savings in immediately positive.

- Non – Integrated Paper Mills

Figure 19: Cost savings by increasing moisture in P, W, X grades at a non-integrated paper mill

For a non-integrated paper mill, the impact of increasing the equilibrium moisture level is higher because water is replacing market pulp (which is \$ 600 / ton). An increase in sheet moisture from the standard 4.5 % to 5.3 % saves from \$ 4.5 / ton to \$ 9.5 / ton. Note that in Figure 19, the cost savings is immediately positive.

Replace Titanium Dioxide (TiO₂) with SNF

Due to the nano-structure of these Silicate Nano – Fibers (length 3-4 microns, thickness 20 nanometers), they scatter light extremely well. The result is that these fibers, which can cost from \$ 450 to \$ 600 per ton, can make a 1 to 1 replacement for TiO₂, which costs \$ 2000 per ton.

Both integrated and non-integrated mills can benefit equally from replacing TiO₂ with SNF. TiO₂ is used in high opaque, light-weight paper and coated papers.

The replacement of 2 % TiO₂ to 10 % TiO₂ could result in savings from approximately \$ 30 / ton to \$ 148 / ton (see Figure 20).

Figure 20: Replacement of SNF for TiO₂ at a paper mill

Increasing Press Solids → Energy Savings

Yet another unique characteristic of SMP is that they can be pressed harder than conventional fillers, but they spring back and do not lose their shape. This allows paper machine to press paper to a higher solids without losing caliper and other paper properties.

Figure 21 shows that as the press solids increase from 35 % to 55 %, the energy savings from not using the energy to drive as much water out of the sheet were computed in the range of \$ 5 / ton to \$ 22 / ton.

Figure 21: Cost Savings as Press Solids is increased

Selling Price Premium

Several customers of paper mills use rolls of paper to print copies of pamphlets, newspapers, flyers, and other items. These customers purchase paper based on the number of impressions they get per ton of paper. Since the basis weight can be reduced by adding SNF into the paper, the customer can get more impressions per ton of paper. These customers are very interested in increasing their impressions per ton and as a result, are willing to pay an up-charge per ton of paper that has this reduced basis weight.

As Figure 22 show, a paper manufacturer can get an additional \$ 45 / ton in revenue just by implementing GRI's materials.

Figure 22: Selling Price Increase as a result of lower Basis Weight

Details of Effect on Paper

Effect of Reducing Basis Weight of Paper

Furthermore, the high performance of patented GRI nano materials produces stronger paper (than market PCC) so it can be manufactured at lower basis weight than normal. Results from pilot paper machine tests have illustrated these trends. The results in Figure 23a are for papers containing 17.5% total nano material. The drying time of paper made at 19 lb / 1300 ft² basis weight using market PCC is compared to paper containing a blend of three GRI nano materials and made at 18 lb / 1300 ft². These two papers have equivalent strength properties. The drying time for paper containing the combination of three GRI nano materials declines by about 23% relative to paper containing solely market PCC.

In addition as shown in Figure 23b at the same 17.5% nano material level, the press solids increase 3% relative to the market PCC. These trends drying time and in higher press solids contribute to the reduction in drying energy.

Figure 23 a and b: Effect of Reducing Basis Weight and Changing Furnish on Drying Time and Press Solids

The manufacturer has the choice to accept the lower steam consumption and fossil fuel burn rate. Alternatively he may increase the machine speed and the production rate by roughly a proportional amount and decrease per unit paper production costs.

The paper nano material content also affects drying time. For example, Figure 24a shows that for papers made at 18 lb / 1300 ft² the reduction in drying time when changing from 22% total nano material to 26.8% amounts to about 40%. Finally Figure 24b shows that under the same conditions the press solids increase by about 18%.

Figure 24 a and b: Effect of Nano Material Level on Drying Time and Press Solids

As shown in Table 14 the impact of pressing, reduced basis weight and increased nano material level are additive. So for the conditions described in Figures 28 and 29, it is possible to improve the paper manufacturing energy efficiency by over 40% while using GRI patented nano materials.

Table 14: Summary of Energy Savings

Effect	Press Solids Increase	Energy Savings
Improved Pressing	9 %	25 %
Reduced Basis Weight	6 %	18 %
Increased Nano Material level	3 %	9 %
Total Potential Energy Savings		43 %

Effect of Increasing Press Solids

Increasing the press solids to over 50% by using this technology could have a profound effect on paper drying energy requirements. As shown in Figure 25 normal paper drying heat loads (for press solids of 35%) amount to about 4×10^6 BTU per ton paper to reach 90% solids. Some older paper machines operate at 35 to 45% press solids while newer machines often operate at between 40 and 50% press solids. For older machines this technology may permit increase in press solids without investing in expensive new press technology. In that case increasing press solids to 50% by installing high filler loading could decrease the drying load to about 2 million Btu/ton paper.

Figure 25: Energy Savings Resulting from Increased Press Solids

But the use of GRI nano material technology could permit further reduction in drying energy. For example by pressing papers containing GRI nano materials to 55% press solids the drying energy may amount to a total of about 1.3×10^6 Btu/ton paper. This would amount to about 67% reduction in drying energy per ton of paper relative to a press operating at 35% solids. Relative to operation at the present limit of 50% solids, that amounts to about 35% improvement in drying load. Exact savings are dependent on site specific factors such as the press technology and other machine related bottlenecks.

Impact on US Paper Industry

Energy Savings

The portion of U.S. fine paper production (P, W, X) that is targeted by this proposal amounts to about 15 million tons per year. Thus, a 50% penetration of that market by this technology could result in an energy savings of about **46.0 trillion BTU per year**. This is equivalent to about **0.64 million barrels of oil per year** as shown below.

Detailed Calculations

Energy Savings due to Value Propositions

% Savings due to Higher Press Solids	25 %
% Savings due to Basis Weight Reduction	18 %
% Savings due to Increased Inorganic Material Level	<u>9 %</u>
Total Potential % Savings	43 %

Energy Savings due to Higher Filler / Higher Solids Paper

Energy to Dry 1 ton paper / paperboard	4 million BTU / ton paper
Energy to Dry High Solids Paper	<u>2.28 million BTU / ton paper</u>
Energy Savings per Paper Tonnage 43 %	1.72 million BTU / ton paper

GRI's Market Penetration

7.5 million tons / year

Energy Savings per Paper Tonnage

1.72 million BTU / ton paper

Total Potential Drying Energy Savings

12.9 Trillion BTU / year

Energy Savings due to Production of Silicates instead of Pulp

Energy to produce 1 ton pulp from trees	20 million BTU / ton pulp
Energy to produce 1 ton GRNSFC fibrous materials	<u>3 million BTU / ton material</u>
Energy Savings for GRI SNF	17 million BTU / ton paper

GRI's Fibrous Fillers Production

1.825 million tons / year

Energy Savings for GRI SNF

17 million BTU / ton

Potential Total Energy Savings by replacing pulp

31.025 Trillion BTU / year

Energy Savings due to Production of PCC instead of Pulp

Energy to produce 1 ton pulp from trees	20 million BTU / ton pulp
Energy to produce 1 ton GRNSFC S-PCC	<u>0 million BTU / ton material</u>
Energy Savings for GRI S-PCC	20 million BTU / ton paper

Note: this is an exothermic reaction

GRI's S-PCC Production

0.75 million tons / year

Energy Savings for GRI S-PCC

20 million BTU / ton

Potential Total Energy Savings by replacing pulp

15 Trillion BTU / year

Potential Total Energy Savings

Energy saved with High Filler Paper	12.9 Trillion BTU / year
Energy saved with Silicate Production	31.025 Trillion BTU / year
Energy saved with S-PCC Production	<u>15 Trillion BTU / year</u>
	46.03 Trillion BTU / year

Reduction of Wood Usage

The innovative Fibrous Fillers described in this proposal can partially substitute (≈50%) for wood fibers with potentially impressive savings in wood fiber and in production costs. At a 50% penetration in the targeted fine paper market and 50% fiber replacement by nano material, the

industry wood demand would drop by about 7.5×10^6 tons per year. Assuming a value of \$600 per ton of bleached pulp and \$450 per ton of nano material, the annual raw material savings would amount to approximately \$1.2 billion, helping to make the pulp and paper industry more competitive in the world market.

Detailed Calculations

Pulp Savings	2.625 million tons paper / year
Number of Trees to make 1 ton paper	<u>14 trees / ton paper</u>
Potential Total # of Trees Saved	36.75 million trees / year

CO₂ Sequestration

The innovative technologies to manufacture S-PCC and SNF nano materials will have major positive impact on the emission of CO₂ from integrated pulp and paper mills and surroundings. These savings originate from two general, quantifiable sources (CO₂ fixation in nano material products) and two site-specific sources (mitigation of CO₂ emitted from vehicle combustion during transport from normally, centrally located PCC production sites and from atmospheric CO₂ sequestered by unharvested trees). On-site generation of Fibrous Fillers and Super PCC will permit separation and sequestration of CO₂ from the paper mill power boiler stack. The reduction in CO₂ emissions are estimated in Table 15.

Table 15: Estimated Yearly CO₂ Reduction

Key CO ₂ Savings	TPY CO ₂ Saved
1.5 Million tons per year S-PCC Produced	660,000
2.25 Million TPY Silicates Produced - Sequestering of CO ₂	79,000
3.75 Million TPY Virgin Pulp Replaced - CO ₂ Not Produced	11,290,000
3.75 Million TPY Virgin Pulp Replaced - CO ₂ Absorbed by Saved Trees	340,000
3.75 Million TPY Virgin Pulp Replaced - CO ₂ from Hogfuel not Burned	3,000,000
Total CO ₂ Saved (CO ₂ Sequestering + Prevention)	15,400,000

Table 24 above shows that if GRI's technology is accepted enough to produce 1.5 million tons per year, this will sequester almost 700,000 tons of CO₂ per year. At the same time, 2.25 million tons of GRI's Silicate nano – material will sequester another 80,000 tons of CO₂ per year. Together, GRI's product will trap about 740,000 tons CO₂ per year that would otherwise leave as greenhouse gases. Table 24 also shows that the 3.75 million tons per year of pulp that has been replaced with GRI's nano – materials will keep over 11 million tons of CO₂ from entering the atmosphere. The fuel that would be burned to generate the energy to pulp 3.75 million tons of pulp is 3 million tons of CO₂. This fuel is also not burned, keeping the CO₂ trapped. Finally, trees (from which pulp is produced) capture CO₂ during photosynthesis. The trees that were not

cut down to produce the 3.75 million tons of pulp will pull over 300,000 tons of CO₂ from the air.

Detailed Calculations

Potential Tons CO₂ Sequestered by Trees

Total # of Trees	36.75 million trees / year
Pounds of CO ₂ sequestered per tree	<u>13 # CO₂ / tree</u>
Potential Tons CO ₂ Sequestered by Trees	0.24 million tons CO ₂ / year

Potential Tons CO₂ Sequestered by S-PCC

Tons CO ₂ sequestered per ton S-PCC	0.44 tons CO ₂ / ton PCC
Tons S-PCC produced	<u>0.75 million tons PCC / year</u>
Potential Tons CO ₂ Sequestered by S-PCC	0.33 million tons CO ₂ / year

Potential Tons CO₂ Sequestered by Silicates

Tons CO ₂ sequestered per ton SNF	0.035 tons CO ₂ / ton Silicate
Tons SNF produced	<u>1.825 million tons Silicate / year</u>
Potential Tons CO ₂ Sequestered by Silicates	63,875 tons CO ₂ / year

Potential Tons CO₂ Savings due to Pulp Production

Tons CO ₂ released per ton Pulp produced	3.01 tons CO ₂ / ton pulp
Tons Pulp replaced by SNF	<u>2.625 million tons pulp / year</u>
Potential Tons CO ₂ Saved by not producing Pulp	7.9 million tons CO ₂ / year

Potential Tons CO₂ Not Released by Burning Hogfuel to Pulp Trees

Total Energy Savings	46.03 Trillion BTU / year
Energy per ton hogfuel	16.7 million BTU / ton hogfuel
CO ₂ produced by burning hogfuel	<u>0.614 tons CO₂ / ton hogfuel</u>
Potential CO ₂ Savings by not burning hogfuel to pulp	1.7 million tons CO ₂ / year

Total Potential CO₂ Savings

CO ₂ Sequestered by Trees	240,000 tons CO ₂ / year
CO ₂ Sequestered by S-PCC	330,000 tons CO ₂ / year
CO ₂ Sequestered by Silicates	63875 tons CO ₂ / year
CO ₂ Sequestered by not Pulping Trees	7.9 million tons CO ₂ / year
CO ₂ Sequestered by not Burning Hogfuel	<u>1.7 million tons CO₂ / year</u>
	10.2 million tons CO₂ / year

Cost Reduction

Value Proposition and Benefits

The uses of “Fibrous and Engineered Nano materials” are many. The main ones are:

- TiO₂ Reduction in High End Paper

- Basis Weight (BW) Reduction in Xerographic Paper
- Fiber Substitution in Xerographic, Offset, and other paper grades.
- Dryer Energy Savings
- Pulp Mill Energy Reduction
- CO₂ Sequestering

The details of how much these technologies can potentially save the US Paper Industry are given below.

Detail Calculations

Potential Savings due to Pulp Fiber Replacement with Silicates and S-PCC

Selling price of Pulp	\$ 700 / ton
Pulp Replaced by GRI's SNF	<u>2.625 million tons / year</u>
Potential Pulp Sale Revenues	\$ 1.837 billion / year

Manufacturing cost of Pulp	\$ 300 / ton
Pulp Replaced by GRI's SNF	<u>2.625 million tons / year</u>
Potential Pulp Manufacturing Costs	\$ 0.788 billion / year

Pulp Sale Revenues	\$ 1.837 billion / year
Pulp Manufacturing Costs	<u>\$ 0.788 billion / year</u>
Potential Increased Income from Pulp Sales	\$ 1,050 million / year

Potential Savings due to Value Propositions

Savings due to Increased Ash	\$ 5 / ton
Savings due to Reduced Basis Weight	<u>\$ 15 / ton</u>
Savings due to Value Propositions	\$ 20 / ton

Market Size affected by GRI's Products	7.5 million tons / year
Savings due to Value Propositions	<u>\$ 20 / ton</u>
Potential Total Savings due to Value Propositions	\$ 150 million / year

Potential Total Economic Benefit

Savings due to Pulp Replacement	\$ 1,050 million / year
Savings due to Value Propositions	<u>\$ 150 million / year</u>
	\$ 1,200 million / year

Conclusion

In conclusion, the benefits for the US Paper Industry are as follows:

- 46 Trillion BTU of energy saved per year
- 36.75 Million Trees remaining standing per year
- 10.2 Million Tons of CO₂ not emitted or sequestered per year
- \$ 1.2 billion per year in cost savings and increased revenue

Other, Non-Paper Commercial Applications of these Unique Nano Materials

While this project focuses on the \$10 billion US fine paper industry, the benefits these pigments could contribute to other industries shown in Figure 31 will be quite substantial. The ability to manufacture synthetic inorganic nano materials with a wide range of particle size, particle aspect ratio and shape, bulk density, surface chemistry and reactivity means that these materials have potentially very broad applications.

MILESTONE STATUS TABLE:

Note: These milestones have been revised from the original proposal due to the current funding revisions, and in view of D.O.E. and AF&PA.'s review of this project.

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			

Task I	GRI Optimization of Manufacture of Silicate Nano-Fibers (SNF, TiSil, or T-8) and Silicate Macro-Particle (SMP, or T-4)			
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Year 1

I-1.1	Lab scale (2.0 gallon reactor) study a) Critical process parameters (temperature, reaction time, etc.) to produce Silicate Nano-Fibers b) Screening of alternate raw materials	12/31/2002	12/31/2002	Completed
I-1.3	First production scale (10,000 gallon reactor) trial a) Manufacture of silicate macro-particles (SMP), employing the optimum process conditions from I-1.2 b) Lab scale characterization and testing of SMP pigment	6/30/2003	6/30/2003	Completed
I-1.4	Second production scale (10,000 gallon reactor) a) Manufacture of silicate macro-particles (SMP) b) Lab scale characterization and testing of SMP pigment	8/31/2003 9/30/2003	8/31/2003 9/30/2003	Completed

Year 2

I-2.1	Empirical process models and response surface analysis employing the technique of designed optimization experimentation (DOE)	3/31/2004	3/31/2004	Completed
I-2.2	Preliminary design for a commercial "Fibrous Filler" plant	3/31/2004	3/31/2004	Completed
I-2.3	Preliminary design for a prototype "Fibrous Filler" plant	6/30/2004	6/30/2004	Completed
I-2.4	Additional production trials using 10,000-gallon reactors (Toll Manufactures)	10/30/2004	10/30/2004	Completed

Year 3

Goal: Commercial Validation of Fibrous and Engineered Fillers Manufacturing (Tech-4, Tech-6, Tech-8, and SPCC)

I-3.1	Lab scale (2.0 gallon reactor) study	3/31/2005		85% Completed Ongoing
	a) Complete process model and optimization for SNF			
	b) Screening of alternate raw materials screening and optimization			

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			
I-3.2	Pilot scale (30 gallon reactor) study	3/31/2005		75% Completed Ongoing
	a) Scale up and verification of lab scale process models			
	b) Scale up with new raw materials			
	c) Repeatability of SMP			
	d) Repeatability of SNF			
I-3.3	Scale-up/optimization and repeatability study on the pilot scale (30-gallon reactor)	3/31/2005		Completed Ongoing
I-3.4	Optimization of Super-PCC (Tech 2) in lab and pilot scale	3/31/2005	8/31/2005	Completed
I-3.5	Detailed design and engineering of prototype plant to manufacture calcium silicates	3/31/2005	6/30/2005	Completed
I-3.6	Lab-scale reactor raw material screening (lime and silica)	6/30/2005	6/30/2005	Completed
I-3.7	Development of a new fibrous filler (Tech 6) for reduced drying energy	6/30/2005	3/30/2006	95% Completed Ongoing
I-3.8	Scale-up of S-PCC manufacturing to the pilot scale.	6/30/2005	6/30/2005	Completed
I-3.9	Prototype plant construction started.	6/30/2005	3/30/2006	Completed
	a) Equipment purchase.			
	b) Business agreements.			
	c) Construction.			
I-3.10	Process models for SMP and SNF and optimize process with alternate raw materials	9/30/2005		35% Completed Ongoing
I-3.11	Process models for S-PCC or Tech-2.	9/30/2005	9/30/2005	Completed
I-3.12	Pilot-scale optimization of alternate lower cost raw materials, process conditions to manufacture, lower cost of silicates (less than or equal to cellulose fiber)	9/30/2005		Ongoing
I-3.13	Preliminary PCC-silicate hybrid work	9/30/2005		Abandoned*
I-3.14	Final Optimization of raw materials, process conditions to manufacture most cost effective high performance silicate products (Nano-Fibers, Macro-Particles)	10/31/2005		
I-3.15	Prototype plant construction complete	10/30/2005	4/1/2006	Completed
I-3.16	Commercial production trials of nano-carbonates (SPCC or Tech-2)	12/31/2005	3/31/2006	Completed

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			
I-3.17	Commercial production trials of calcium silicates for papermaking	12/31/2005	12/31/2006	90% Completed
I-3.18	Ramp time and soak time influences at the pilot-scale.	1/31/2006		Completed
I-3.19	Detailed design and engineering of commercial plant to manufacture calcium silicates (Phase II)	12/31/2005	12/31/2006	Ongoing
I-3.20	Scale of Manufacturing of Silicate Macro Particles	9/30/2007		Ongoing
I-3.21	Develop Low Energy using Silicate Micro-Fiber (Tech-7)	9/30/2007		Ongoing

Task II	(Lawrence Livermore National Laboratory) To study and elucidate the mechanism of Silicate Nano-Fiber and Silicate Macro Particle formation
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Project task with LLNL cancelled.

Year 1

II-1.1	Characterization of GRI's Silicate Nano-Fibers (SNF)	9/30/2003		Completed
II-1.2	Lab preparation of GRI standard silicate products (SNF or T-8) in LLNL reactors	12/31/2003		Unable to complete
II-1.3	Chemical and phase analysis of the reaction products as a function of time throughout the process of synthesizing Silicate Nano-Fibers	12/31/2003		Completed
II-1.4	Special test to characterize silicate products using atomic force microscopy (AFM), Vertical scanning interferometer	12/31/2003		Not Completed

Year 2	Goal: Optimization			
II-2.1	Preliminary mechanism of "Fibrous Filler" formation	6/30/2004	6/30/2004	Not Completed
II-2.2	Study the effect of impurities on formation of silicates	6/30/2004		Not Completed
II-2.3	Review LLNL's progress by GRI	6/30/2004	6/30/2004	Completed
II-2.4	Study the alternate lower cost raw materials, silica, lime source for T-8 Silicate Nano-Fibers (SNF)	6/30/2004		Not Completed
II-2.5	Review LLNL's progress with DOE	9/31/04	9/31/04	Completed
II-2.6	Process modeling using thermodynamic database and kinetic database available at LLNL	10/31/2004		

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			
II-2.7	Preliminary preparation of GRI's standard silicate macro-particles (SMP) in LLNL reactors and repeat task II-1.1 and II-1.2	12/31/2004		
II-2.8	Improving the process of manufacturing silicate products by employing catalysts, etc.	12/31/2004		

Year 3		Project Task Cancelled		
II-3.1	Pennsylvania State University: Characterization of mechanism of formation of fibrous filler.	6/30/2005		
II.3.2	Final kinetic and thermodynamic models to support design of commercial plant	9/30/2005	6/30/2006	

Task III		(GRI and Paper Companies) Development of Ultra-High Ash Paper (Up to 50% Calcium and Silica Based Fillers)		
Year 1				
III-1.1	First commercial paper machine trials	7/31/2003	7/31/2003	Completed
III-1.2	Evaluate paper manufactured during production trial (both in lab and in field)	9/30/2003	9/30/2003	Completed
III-1.3	To study the effect of high "Fibrous Filler" (25%-50%) content on paper properties and paper processes (combination of silicate nano-fibers and macro-particles)	12/31/2003	12/31/2003	Completed
III-1.4	Second and third commercial scale paper machine trial	11/30/2003	11/30/2003	Completed
III-1.5	Preliminary system wide energy audit comparing existing pulp and paper mills vs. future mills with GRI "Fibrous Filler" on site plants	12/30/2003	12/30/2003	Completed
Year 2				
III-2.1	Preliminary system wide energy audit comparing existing pulp and paper mills vs. future mills with GRI "Fibrous Filler" on site plants	3/31/2004	3/31/2004	Completed
III-2.2	Paper machine productions trials	10/31/2004	10/31/2004	Several trials completed
III-2.3	Screen new wet end additives to enhance sheet strength	12/30/2005		

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			

Year 3		Goal: Validation of Technology of Fibrous/Engineered Fillers		
III-3.1	Study the effects of pressing on drying energy	3/31/2005	3/31/2005	Completed
III-3.2	Pilot paper machine trial to evaluate Super-PCC, SMP, and SNF in Germany	3/31/2005	3/31/2005	Completed
III-3.3	Paper quality / performance (printing, dusting)	6/30/2005	12/31/2006	80% Completed Ongoing
III-3.4	Paper machine trial of S-PCC.	6/30/2005	6/30/2005	Completed
III-3.5	Energy reduction in papermaking processes due to:	6/30/2005		85% Completed Ongoing
	a) Higher pressing and lower drying	12/30/2005		
	b) Lower refining of SMP and SNF			
III-3.6	Study the effect of pigment on strength additives, internal sizing, etc.	9/30/2005	12/31/2006	70% Completed Ongoing
	a) Lab-scale evaluation			
	b) Pilot paper machine evaluation			
III-3.7	Screen new wet end additives to enhance sheet strength and retention	9/30/2005	12/31/2006	70% Completed Ongoing
III-3.8	Confirm value propositions –TiO ₂ reduction, basis weight reduction, increase in ash (fiber replacement)	9/30/2005	12/31/2006	75% Completed Ongoing
III-3.9	New value added paper product development (e.g., inkjet paper, 40% filler composite)	12/30/2005		Abandoned*
III-3.10	Study the mechanism of fiber to Silicate Nano-Fiber bonding at higher ash levels (20-50%)	12/30/2005		20% Completed, Abandoned*
III-3.11	Commercial paper machine production using commercially produced silicate “Fibrous Filler” (nano-fibers, macro-particles)	12/30/2005	12/31/2006	75% Completed Ongoing
III-3.12	Field trial of paper produced with commercially produced T-4 and T-8	12/31/2005	12/31/2006	75% Completed Ongoing
III-3.13	Full life cycle analysis of existing pulp and paper mills vs. future pulp and paper mills with GRI “Fibrous Filler” on site plants	3/31/2006		Abandoned*

<i>ID Number Scheme: Task - Year. Subtask</i>		Planned Completion Date	Actual Completion Date	Comments
ID Number	Task / Milestone Description			

III-3.14	Electrochemical charge neutralization in paper	6/30/2006	12/31/2006	Abandoned*
Year 3		Goal: Validation of Technology of Fibrous/Engineered Fillers		
III-3.1	Study the effects of pressing on drying energy	3/31/2005	3/31/2005	Completed
III-3.2	Pilot paper machine trial to evaluate Super-PCC, SMP, and SNF in Germany	3/31/2005	3/31/2005	Completed
III-3.3	Paper quality / performance (printing, dusting)	6/30/2005	12/31/2006	80% Completed Ongoing
III-3.4	Paper machine trial of S-PCC.	6/30/2005	6/30/2005	Completed

Task IV	(Western Michigan University) Optimization of surface treatment formulations (S. Abubakar, M. Joyce)
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Task completed.

Year 1

IV-1.1	Determine the compatibility of starch, PVOH binders and silicate pigments	6/30/2003		Completed
IV-1.2	Maximize coating solids using five different binders	6/30/2003		Completed
IV-1.3	Determine minimum pigment-binder ratio for inkjet print quality	9/30/2003		Completed
IV-1.4	Study the effect of temperature and solids on silicate coatings	9/30/2003		Completed
IV-1.5	Study the dry coating structure, ink density comparison with silica gel	9/30/2003		Completed
IV-1.6	Study absorptivity and surface energy of Silicate Nano-Fibers and silicate macro-particles using contact angle measuring device and methods to improve print densities	12/31/2003		Ongoing
IV-1.7	Analyze data and submit report – TASK ON HOLD	12/31/2003		Completed

Year 2		Goal: Size press study to characterize dry coating structure		
IV-2.1	Lab scale Optimization of coating formulation using GRI's fibrous fillers, binders, water fasteners, etc.	6/30/2004		No Other Work
Year 3		TASK ON HOLD		
IV-3.1	Comparison of optimum formulation with other pigments	6/30/2005		No Work
IV-3.2	Pilot coater (cylindrical lab coater)	6/30/2005		No Work

	a) Application of optimum coating formulation on a pilot CLC coater			
IV-3.3	Analyze the data and final reports	9/30/2005		No Work

*No Funding Available.

**New Task.

BUDGET

The total approved budget for this project was \$ 3,000,000. GR International and its partners had committed 20 % as cash or in-kind support to the amount of approximately \$ 975,000 of the original \$ 3,000,000. \$ 270,000 was directly allocated to Lawrence Livermore National Laboratory to carry out the research in elucidating the mechanisms of Fibrous Filler formation (Task II). Western Michigan was funded for \$ 26,000. Their task was to study the use of Fibrous Fillers in coatings (Task IV). At the end of 2008 Q3, GRI had spent \$ 2,195,844. Actual recipient expenses (both cash and in-kind) was \$ 1,833,222. Thus the total project expense was \$ 4,029,066. GRI and its partners' contributed approximately \$ 600,000 more than the minimum required by the DOE. There were no expenses under this project since Q3 of 2008. For the details of the budget, see Tables 16 and 17 below.

Budget Data (as of September 31st, 2008):

Table 16: Budget Data

Project Spending and Estimate of Future Spending							
Quarter	From	To	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share of Outlays	Actual Recipient Share of Outlays	Cumulative
	Start	9/30/04	Note 1	834,325	Note 1	549,600	1,383,925
4Q04	10/1/04	12/31/04	175,000	136,861	75,000	158,922	1,679,708
1Q05	1/1/05	3/31/05	175,000	147,797	75,000	39,200	1,866,705
2Q05	4/1/05	6/30/05	175,000	158,061	75,000	39,200	2,063,966
3Q05	7/1/05	9/30/05	175,000	155,009	75,000	141,100	2,360,075
4Q05	10/1/05	12/31/05	175,000	139,734	75,000	39,200	2,539,009
1Q06	1/1/06	3/31/06	175,000	119,952	75,000	199,200	2,858,161
2Q06	4/1/06	6/30/06	0	98,820	75,000	159,200	3,116,181
3Q06	7/1/06	9/30/06	0	45,325	75,000	159,200	3,320,706
4Q06	10/1/06	12/31/06	0	39,629	75,000	79,200	3,439,535
1Q07	1/1/07	3/31/07	0	33,801	75,000	79,200	3,552,536
2Q07	4/1/07	6/30/07	0	58,126	75,000	40,000	3,650,662
3Q07	7/1/07	9/30/07	0	34,062	75,000	40,000	3,724,724
4Q07	10/1/07	12/31/07	0	41,701	75,000	40,000	3,806,425
1Q08	1/1/08	3/31/08	0	34,378	75,000	40,000	3,880,803
2Q08	3/1/08	6/30/08	0	44,818	75,000	30,000	3,955,621
3Q08	7/1/08	9/30/08	0	73,445	75,000	0	4,029,066
4Q08	10/1/08	12/31/08					
1Q09	1/1/09	3/31/09					
Totals			2,100,000	2,195,844	1,200,000	1,833,222	4,029,066

Table 17: Overview of Budget Breakdown

			Approved Spending Plan			Actual Spent to Date		
Phase/Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	04/03	03/04	700,000	300,000	1,000,000	537,415	399,000	936,415
Year 2	04/04	03/05	700,000	300,000	1,000,000	581,568	348,722	930,290
Year 3	04/05	03/06	700,000	300,000	1,000,000	572,756	418,700	991,456
Year 4	04/06	03/07	0	150,000	150,000	217,575	476,800	694,375
Year 5	04/07	03/08	0	0	0	168,267	160,000	328,267
Year 6	04/08	03/09	0	0	0	118,263	30,000	148,263
Totals			2,100,000	975,000	3,075,000	2,195,844	1,833,222	4,029,066