

Review Article

In-Situ Precipitated Calcium Carbonate Paper Filler Material – A Review

ABSTRACT

Since the invention of the paper by in 105 CE to Chai Lun many improvements have been made to the paper product we know today. Today a paper machines can be over 600 m long and 11.5 m wide, running at speeds of over 2000 m/min, and producing up to 4,500 metric tons per hour. Paper as we know it today, can be characterized as an orthotropic thin plate with a thickness of over 500 μm and a basis weight of over 500 g/m^2 requiring additives to achieve the needed paper properties.

Calcium carbonate based filler additive materials have approximately 70% market share in North America, and can be added to a maximum of 20 to 25% based on fiber material.

In the 1970s a shift from acid to neutral papermaking started which made it possible to use precipitated calcium carbonate in the paper manufacturing process. New printing technologies required paper with superior properties. This led to an increase in filler content and specially designed filler particles. The in-situ precipitation and filler manufacturing processes are known today, can be divided into (i) mechanical method which uses high shear and centrifugal forces to load the fiber pores with the filler particle, (ii) a chemical method which is the common method in producing precipitated calcium carbonate in a solution since the 1980's for papermaking applications, and (iii) a combination of the mechanical and chemical method which precipitates the calcium carbonate particles on and into the fiber material present in the solution.

All research on various in situ precipitation processes, including patented technologies, since the 1970's showed that the achieved handsheet properties have higher brightness and opacity values as well as a coarser surface structure, lower smoothness and gloss. In-Situ processes showed improvements for the paper manufacturing process in regards to physical and mechanical handsheet paper properties.

However, no commercial applications of this process have been found at present time. However, mixing the filler particles with the pulp suspension and storing this suspension in the headbox feed chest, for a specific time, applies indirectly in-situ principles in today's paper making process operations.

Keywords: In-situ precipitation, calcium carbonate, filler, GCC, PCC, papermaking,, printing, fiber loading, filler loading

1. INTRODUCTION

Paper products have been used since millenniums as a form of communication and preservation. The timetable of papermaking begins in Egypt around 3500 BC. Papyrus artifacts with written characters were found in Egyptian tombs dating back to 3500 BC [1,2]. The Egyptians used a tropical, grass-like swamp plant (Latin: *Cyprus Papyrus*) as their raw material. The type of paper was a woven paper like material, manufactured, by first cutting the plant into strips, then wove the strips together, and finished with mussel shells or animal

teeth to create a smooth writing finish [2] This type of paper was used by, Egyptians, Greek and Romans for record keeping, art and religious matters. The documents were usually kept as a roll type document [3]. In 200 CE the Mayans produced a similar paper out of bark. This paper was used primarily for clothes and ritual objects [3]. In France and Germany permanent paper made of animal skin was introduced and reached its highest popularity during the Middle Ages, around 1500 CE before it was eventually replaced by paper products [4, 5].

The origin of paper dates back to ancient China around during the Eastern Han Dynasty (25-220 CE). The invention of the papermaking art was granted in 105 CE to Chai Lun, an eunuch, overseeing at that time the workshop of the Imperial Court, producing very supply needed, from daily used items to weapons [3,5].

The Art of Papermaking was kept as a secret, and it ended up eventually in Japan 500 years later. It took over one millennium, since its invention to reach the European continent and another 500 years to spread all over Europe, to Mexico, the US and Canada [1,6].

The traditional art of papermaking is still used today in countries such as China, Japan, Thailand. The paper is more commonly made out of bast fibers from the mulberry tree (*Broussonetia Papyrifera*) or the Khoi tree (*Streblus asper*) [3] These papers are very versatile and are used in a variety of products including gift wrapping, paintings, book bindings, greeting cards, wallpaper and architectural and interior design applications.

All over the world the traditional way of hand making paper is preserved by museums and companies that focus on the traditional way of papermaking. In the U.S. for example: Friends of Darth Hunter, a non-profit organization, preserves the art of handmade paper and bookmaking [7].

Over time the art of papermaking evolved and led to the replacement of animal skin parchment, the dominant writing material at the time [1]. The invention of the printing press in 1446, by Gutenberg (1400-1468) was one of the most significant inventions that changed the art of printing, by using removable metal type [1]. The demand of printing material grew and overtime parchment made from animal skin was replaced with paper [10].

Paper was still a laborious process. Some processes were mechanized and improved over generations. However, the laborious process of paper sheet forming using a sheet mold containing a screen as support structure for the forming paper sheet did not changed [1,3, 10].

Driven by the need to produce a paper sheet of greater length, allowing not to glue individual sheets together for the production of wallpaper, led to the invention of the first endless-wire paper machine by Nicolas Louis Robert (1761-1828) in 1799 [1,3,10]. From there on paper could be produced in large quantities.

In England the paper making entrepreneur brothers Henry (1766-1854) and Sealy (1773-1847) Fourdrinier build the first continuous operating machine incorporating a forming table in 1808 with a width of 76 cm in 1883 and shortly thereafter a machine with a forming width of 152 cm.

These new inventions provided the ability to produce an endless paper material at the beginning of the 19th century. As a result fiber material produced from rags (recycled cloth) came in short supply and other fiber sources had to be found. In 1859 fibrous material mechanically ground from wood was introduced for papermaking using a spindle wood grinder by the company Voith [1, 10]. The process was invented by Fridrich Gottlob Keller (1816-1895) in 1843 [11].

Chemical pulping processes were invented shortly thereafter. The first process was the soda process developed by Charles Watt and Hugh Burgers in 1851 [11-12]. In this process lime is used to produce calcium bisulfate liquor which is capable of dissolving cellulose wood elements. The first pulp mill using the sulfate was built in Philadelphia near the Schuylkill River using poplar as raw material in 1852. However, the sulfate process turned to be a rather expensive process due to the production of sodium carbonate from sodium sulfate [1]. Carl Ferdinand Dahl from Danzig, Prussia, Germany got the first US Kraft patent, No.

296,93,5 issued in 1884 [9]. The Kraft process introduced sodium sulfate directly into the recovery process, where sodium carbonate is treated with lime to regenerate the caustic soda. This led to cooking liquors containing sodium sulfate and caustic soda. The result was a stronger but darker pulp. The first pulp mill was built in 1890 in Sweden [14]. From there on the papermaking process of preparing the fiber material as well as machinery needed to produce paper has been continuously improved. The Kraft process is today the most favorable industrial pulping process for producing paper fiber material from wood [11-12].

Paper as we know and use it today, can be described in generally as an orthotropic thin plate having a thickness that ranges from 40 μm to over 500 μm and a basis weight from under 15 g/m^2 to over 500 g/m^2 depending on the paper end product and its application as a writing or printing material, packaging (board) material or, tissue product [6].

Each paper product has its own unique requirements in regard to mechanical integrity, surface topography, optical appearance and printability based on its use and printing process applied [6].

Today's paper products are produced from extracted cellulose fibers from hardwood (leave) and softwood (needle) trees and or recycled paper fiber material, which can contain a mixture of hardwood or softwood cellulosic fibers materials. Other materials such as filler materials, color pigments and other chemical additives might be added based on the specific product requirements [6,15-16].

The machines paper is produced on, can be over 600 m long, and are marvels of technology. Each machine is designed to the individual paper product requirements. Paper machines today can operate at speeds of over 2000 m/min producing a paper sheet with a width of over 11.5 m at daily production rate of over 4,500 tons [17-18].

Today there are worldwide over 400 million tons of paper produced [19]. Consumption of paper products can be used to assess a countries wealth. Leading industry nations such as the U.S. and Germany use over 202 kg and 250 kg of paper per person per year whereas emerging counties such as China are below 70 kg per person per year [19-20]. A potential increase in the rate of paper consumption will be controlled by the market for paper goods over the next years and decades. Paper products have been rediscovered as a sustainable, biodegradability, and eco-efficiency packaging material replacing plastic packaging that might end up as micro plastics in the oceans [21].

Paper and cardboard production reached nearly 78 million metric tons in the US and about 420 million metric tons worldwide in 2019 with an estimated market value of over 83.5 billion dollars in the US [19]. According to the American Forest and Paper Association (AFP) the US paper industry is among the 10 top manufacturing employers in 45 states employing nearly 950,000 people and supporting over one million jobs through the supply chain [22].

According to the U.S. Department of Commerce [23] consumer spent in 2016 nearly 390 billion on E-Commerce. Since then, spending has more than doubled. Consumers spent nearly \$792 billion on the web for retail purchases in 2020, a roughly 32% increase compared to \$598 billion in 2019 [19]. Forecasts for 2021 are above 930 billion and for 2022 to reach on trillion dollars [19, 23].

The steady increasing internet sale and boost through the pandemic years in 2020 and 2021 resulted in a boost of board and packaging products requiring producers to expand their production capacities. For example, the US container board production has increased in 2021 by 5.6% for the ninth time in 10 years [22]. This triggers companies to invest in new locations and machinery. For example: Nine Dragons one of the world largest paper-based manufacturer headquartered in China acquired in 2018 two board mills in Wisconsin and Maine and has invest over 300 million dollars in upgrades during 2019 and 2020 [24]. Palm the larges family-owned paper manufacturing business in the paper industry located in Germany invested over 500+ million Euro in a new board production site producing 750,000 metric tons of board product annually [25-26]. Green Bay Packaging in Wisconsin invested in a new production facility 500+ million dollar to produce paper board products. The plant started producing paper board products in March of 2021 [27].

During the past three decades, the paper industry around the world has experienced significant challenges. Implementation of New technologies is needed due to more stringent environmental laws, ever increasing energy cost, high competitiveness by globalization, and increasing pressure on commodity grades profit margins requires the paper industry worldwide to look out for new ways to cut production cost. [28-29].

In 2018 roughly 420 million metric tons of paper products were produced [19]. To save production costs paper mills have to implement less expensive raw materials and additives to replace more expensive fiber materials. In the 1970's paper manufacturer shifted from acid to alkaline papermaking processes in Europe followed by North America in the 1980's [1]. Since then Precipitated Calcium Carbonate (PCC) has become the preferred filler material for printing and writing grades in paper industry sector [15]. At present time paper products require worldwide over 8 million tons of filler material [30].

The major paper fillers used in papermaking are Ground Calcium Carbonate (GCC) and Precipitated Calcium Carbonate (PCC). PCC is the largest category of filler in North America, with nearly 70% of the market share. The second most common filler type, with a market share of 15%, is Kaolin, followed by ground calcium carbonate (GCC) with 13%. Titan dioxide's estimated market share is about 2%. The use of Silica / Silicates accounts for 0.3% and Talc and Aluminum Trihydrate together account for approximately 0.1% [7].

However, the PCC filler level is limited to a maximum of 20 to 25% depending on the paper grade used.

The use of fillers, especially GCC and PCC, is mainly driven by production cost issues, because paper

Today fillers materials are less expensive than fiber, allowing reduced production costs, improved optical paper properties, dimensional stability, and better sheet formation and printability as well as increased machine speed on the paper machine and coating application side [31]. However, Applying filler material causes a decrease of the paper's strength, increases use of sizing and wet end agents, can create dusting problems and can lower the paper sheets product quality. [29,30,31]. Another serious problem is the loss of bulk and an increasing density of the paper product if filler levels are increased in paper product, because paper is sold in rims and pounds, meaning customers would get less paper product for the same price.

Over the last decades and today the paper manufacturers attempted to increase the calcium carbonate based (CaCO_3) filler in a sheet of paper because of: lower materials costs (calcium carbonate has lower cost than virgin pulp), lower operation costs (less energy consumption in the dryer step), and the improvement of some quality properties (opacity, brightness and printability) (Deng, Zhao, & Ono, 2005) [32]. Associated production cost savings can reach over \$ 4.0 for each 1% increase in filler content [33].

In commercial paper making applications GCC and PCC is presently applied in slurry or powdered form to the papermaking suspension in the blend chest in wet-end section of the paper mill and at the fan pump shortly before the fiber suspension is entering the paper machine headbox after which the sheet forming process occurs [32]. During sheet formation filler particles are incorporated into the paper web. A common problem of both filler types is that a high portion of the colloidal solid filler particles is not retained in the fibrous web due to many factors affecting their retention. [34]. It is known that filler particles incorporated into the paper sheet can cause damage to rotating parts of the paper machine, especially wires and felts and rolls. Filler particles draining through the wire can cause abrasion, plugging and wear, making wire and felts more vulnerable to structural and dynamic damage. However, an increase in filler lever increases the wear on rotating paper machine parts especially wires and felts. These problems in the paper manufacturing process can be particularly serious during production of relatively lightweight papers, as well as copy and printing papers and general papers with a high calcium carbonate filler level [35]. Wear tends to be higher using GCC rather than with PCC particles and is especially

very high using any filler type that incorporates silica and or titan dioxide due to the hardness and abrasive character of the particles.

The use of fillers in the paper manufacturing process is driven mainly by the printing industry's need for higher quality, brightness and improved printability as well as increased machine speed on the paper machine and coating application side. This development is tailoring of course a need of improved coating pigments suitable for increased quality, machine speed and production [35,37-40]

The availability of multicolor offset printing machines has made it possible to economically print small paper tonnage with a high quality print image. In turn, the paper industry's answer to these printing needs has been an increase of filler content in the paper and the use of calcium carbonate as a coating pigment. The two most common user applications of calcium carbonate in the U.S. are coated papers (wood-free 135 g/m²) with a filler level of up to 50%, and copy and office papers (75-80 g/m²) with up to 30% filler level reported [41].

2. PAPER OF TODAY AND THE FUTURE

Constant improvements on the machine and fiber furnish side are taking place today. The search for new fiber resources, more efficient production methods and higher usage of recycled fibers are top priorities in the paper industry, while search for better production methods that increase the overall performance of a paper mills investment continues. The following gives an overview of the filler manufacturing methods currently used and In-situ methods investigated that have the ability to enhance the overall paper making process performance and efficiency if implemented in commercial applications.

2.1. Paper Application for Fillers:

Today, increasing filler level of a paper product is of specific interest, because it fosters energy and environmental benefits due to less wood pulp material, used and therefore generating energy savings in processing and manufacture of paper.

Applications in commodity products such as copy paper were targeted for applications [15]. In the past the availability of multicolor offset printing machines has made it possible to economically print small paper tonnage with a high quality print image. In turn, the paper industry's answer to these printing needs has been an increase of filler content in the paper and the use of calcium carbonate as a coating pigment. The two most common user applications of calcium carbonate in the U.S. are coated papers (e.g. wood-free 135 g/m² with a filler level of up to 50%), and copy and office papers (e. g. 75-80 g/m² with up to 30% filler level reported) [38].

Another application for calcium carbonate fillers is lightweight high-opacity copy and printing paper, a subsection of uncoated fine paper. Different paper grades for lightweight printing and low weight offset papers can be either surface-sized using a size press and starch or pigmented with a coating pigment containing PCC. The basis weight can range between 35-80 g/m² and the filler content can range from 10 to 30% based on the geographic location. For example, in North America, filler levels of 15% are common for basis levels of up to 75 g/m²

Other user applications include paper mills specializing in lightweight coated (LWC) papers with a basis weight of 35 to 80 g/m² and a coating pigment level as high as 30% of the basis weight. These LWC papers are "fiber-limited", which means that the paper mills are trying to reduce the Kraft fiber content in the base sheet by increasing filler levels.

Advertising on boxes has increased the brightness requirements of mottled linerboard grades. These board grades are containing unbleached or bleached fibers in the top ply of the board. The applied fillers in the top ply are causing the wire abrasive ground calcium carbonate to be replaced with PCC.

All these applications have made PCC the primary filler and coating pigment for today's coated and uncoated papers in North America, while in Europe GCC most commonly from marble but to a lesser extent, limestone and chalk is the primary filler material. In order to compete with the existing filler technology a new filler type must show equal or better results in paper performance and process. However, the PCC filler level is limited to a maximum of 20 to 25% depending on the paper grade used, However, filler level of 30% have been reported.

Advertising on boxes has increased the brightness requirements of mottled linerboard grades. These board grades are containing unbleached or bleached fibers in the top ply of the board. In some instances the applied fillers in the top ply are causing the wire abrasive ground calcium carbonate to be replaced with PCC. All these requirements have made PCC the primary filler and coating pigment for today's coated and uncoated papers. Ground calcium carbonate is mostly manufactured from marble but to a lesser extent, limestone and chalk have also earned the acceptance of important segments of paper production [42].

2.2. Calcium Carbonate Based Filler Manufacturing Practice

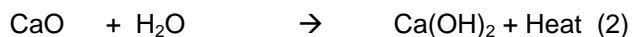
Today's practice in manufacturing PCC and GCC filler particles differs and is adjusted to the individual needs of the paper manufacturing operation and the quality of the paper produced. Figure 1. shows a simple process schematic for GCC and PCC manufacturing. For all paper filler materials it is important that the used raw material allows manufacture a filler material with the needed optical properties. For calcium carbonate filler materials an adequate source of chalk, lime stone and or marble is required to achieve whiteness and brightness properties needed for the produced paper product incorporating the calcium carbonate filler material. Prior to GCC and PCC applications chalk became the first calcium carbonate filler material, because to its natural occurrence a fine dispersed material, whiteness, process ability, good coating ability, plate like structure, low wear to equipment, and minimized health risks [42]. All calcium carbonate based materials have a mining process in common that extracts the material from a quarry containing a chalk, limestone and or marble deposit. The quarried material is crushed and classified. Before used for the individual processes.

For manufacturing PCC the three additional steps are required prior to precipitating the calcium carbonate. First, the quarried lime stone is calcined (burned) in a lime kiln under temperatures around 900°, as shown in equation (1), creating calcium oxide (CaO) and gaseous CO₂ which can be later used to precipitate calcium carbonate if PCC is the desired product.

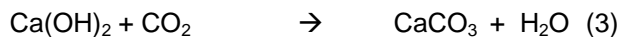


The calcination process temperature chosen can alter the properties of the quicklime. Soft-burned quicklime is formed at lower temperature and shorter calcination time. This quicklime has more pores compared to the limestone. These pores increase the surface area of the quicklime and therefore, increase the reactivity to other chemicals. Hard-burned quicklime is formed by elevated temperature or longer burning time. This quicklime forms larger pores, smaller surface area and is less reactive to other chemicals.

After calcining the CaO product, also called quick lime, is milled, classified and ready to be used in a process, called lime slaking that hydrates the quick lime as shown in equation (2).



During the hydrating process, heat is released and Calcium Hydroxide Ca(OH)₂ is formed. The hydrated lime product is classified, dried and shipped in bulk to further processing or can be directly used to precipitate PCC in a reactor like tank by adding CO₂ as shown in equation 3.



The needed CO_2 is bubbled under mixing into the reactor forming the PCC. CO_2 can be purchased from a gas manufacturer, reused from a mill site combustion process, integrated calcination kiln from an integrated Kraft pulp manufacturing process, or integrated lime kiln at a PCC manufacturing plant.

After precipitation, the PCC is screened, thickened and pumped to an intermediate storage vessel for further use in the paper manufacturing process if the PCC manufacturing plant is integrated and or operated as a satellite plant adjunct to the paper mill.

The GCC manufacturing process does not include the above process steps for precipitation. Instead a dry and wet milling process, combined with washing, classification is used to manufacture GCC particles. The size range for calcium carbonate based filler materials can be in a size range of 0.20 μm to 10 μm based on the application as coating or filler material [42]. In general, the manufacturing process of calcium carbonate based filler materials includes a thickening, drying and bagging process, which allows to send filler material to paper mills that do not have the size to justify a large filler preparation system and or an on-site PCC manufacturing plant. In addition, filler particles can be suspended in a water solution, using dispersion agent to achieve a consistency of approximately 78% [44].

Satellite plants for producing PCC often exist near large-scale paper mills producing mostly graphic printing and writing paper grades. Only paper mills producing 700 metric tons per day have sufficient demand to justify the capital investment of over \$20 million for a satellite plant [1,44-46].

Besides the satellite plant operation, wet and dry ground precipitated calcium carbonate (GCC) with an minimum mean particle diameter of 0.20 μm to 10 μm for dry ground are used to achieve the same effect as PCC. A common problem of both filler types is that a high portion of the filler particles is not retained in the fibrous web, creating wire wear and lower retention [42].

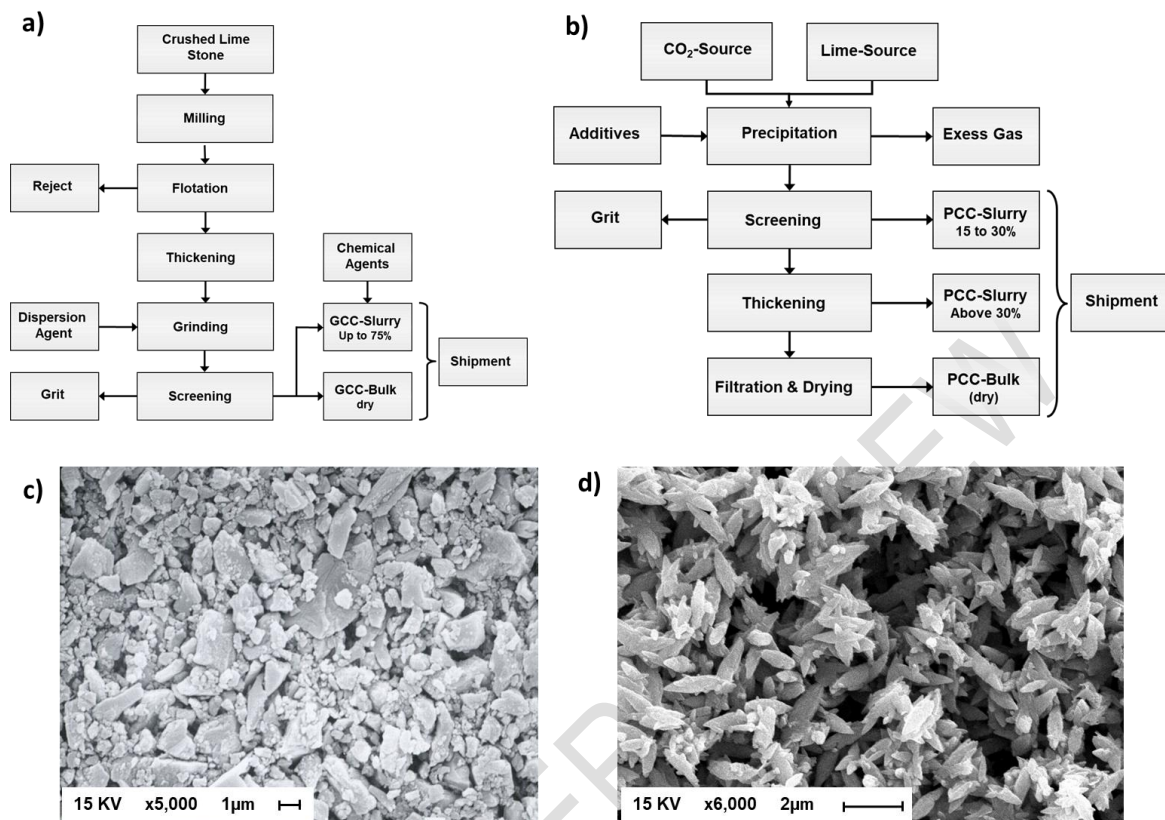


Fig. 1. a) GCC and b) PCC manufacturing schematic, c) GCC particles, d) PCC particles [47]

3. BRIEF REVIEW OF THE STATE OF THE ART

Some of the first United States patents on grinding and precipitation of calcium carbonate for industrial uses were granted in the 1920's [48,49] mostly for use as low cost paint filler and pharmaceutical agent to produce products at lower cost.

In paper manufacturing optical and mechanical properties, increased filler retention during the web forming process, formation and printability are of particular interest.

In addition, filler levels are limited due to mechanical restrictions of the paper produced. Currently, new processes are being developed by the major filler producing companies both for the PCC/ GCC market using chemicals as fixing agents and/or other filler materials to eliminate the known problem of high filler loss by retention. Up to now none of the processes has been commercialized.

One other approach for example is shown by G.R. International investigating a silicate and calcium based filler for paper manufacturing suitable for ash contents over 40% using a pressurized carbonation system. Results publicized show some improvements but do not reveal the needed breakthrough for commercializing. [50-53].

Another approach that was developed started with mixing and soaking the fibers in a sodium sulfate, sodium carbonate, barium chloride and calcium chloride soluble salt solution. The fiber-salt suspension is then added to a barium chloride, calcium chloride and sodium carbonate solution. Through chemical reactions, the pigment particles are precipitated inside the fiber pores. Upon examination, the barium sulfate, barium carbonate and calcium carbonate particles were found to be precipitated and present within the fiber pores [54-55].

The filler level achieved was reported between 2% and 5%, depending on the reactants used.

A multi-pigment strategy is being investigated by most of the filler producing companies with different pigments, e.g. kaolin that has fine plate shape in combination with GCC particles. It is anticipated that these new designed filler materials increase mechanical and optical paper properties and current GCC filler materials can be replaced in the future at a higher filler level [53,56].

Another process called Lumen Loading retains colloidal particles in the porous structure of cellulosic fibers. The resulting fiber slurry has an average of 3 to 8% solid fiber content in the solution. This method uses mechanical, high shear and centrifugal forces to load the fiber pores. In various research reports, the loading process of titanium dioxide under acidic conditions was reported as an absorption process, with the time rate of loading determining the resulting particle concentration [56-60].

A combination of the mechanical and chemical method was first developed at the United States Department of Agriculture (USDA) Forest Products Laboratory (FPL). In this method, hydrated lime is added to fibrous materials at a level of up to 50%. The hydrated lime is deposited in both the water and the fibrous material. Carbon dioxide (CO_2) gas at a level sufficient for chemical reaction is added to the solution of the fibrous material. Under high shear mixing, the gas reacts with the slurry to precipitate calcium carbonate (CaCO_3) in the fiber walls and in-between the fibers. The produced pulp slurry is then forwarded to the paper manufacturing process [61-67].

At the Helsinki University of Technology, research was conducted on the precipitation of filler material to the pulp fines which are actually of the same size as the filler material itself. In addition, Fiber Loading research was performed, showing the feasibility of using an aluminum compound to replace GCC. In this process, pulp fibers with approximately 15% consistency were mixed with a solution of alum. Sodium silicate and sodium hydroxide were added to the slurry by mixing over time [68].

The in-situ precipitation processes known today, can be divided into three categories: a mechanical method, a chemical method and a combination of the mechanical and chemical methods.

4. IN-SITU MANUFACTURING METHODS

4.1 Past and Present Research

With the introduction of paper filler materials for cost saving and paper quality reasons, starting in the 1970's [1] and the development of the precipitation technology for calcium based filler materials along that time, many routes and options of producing filler particles have been investigated. There is a limited amount of published information, especially of technologies that are used commercially due to intellectual property concerns. This information is kept as trade secrets and is not published or protected by patents. Many of the investigated processes on how fillers particles, specifically calcium carbonate and other materials such as titanium dioxide, are attached onto and into pulp fibers is not completely understood. Various researchers have contributed to the filler technology development on how to attach and retain colloidal particles in and on the porous structure of cellulosic fiber, as well as in the liquid containing the cellulosic fibers, categorized in an mechanical, chemical and combination processing method of filler manufacturing.

4.2. The Mechanical Method

The mechanical method uses high shear and centrifugal forces to load the fiber pores. In various research reports the loading process of titanium dioxide under acidic conditions was reported Middleton & Scallan as an absorption process with the time rate of loading determining the resulting particle concentration [69-73]. The opposing surface charges on the fiber and the filler particles create an attraction between them. A washing step eliminates

particles outside the pores. The loaded fibers are then ashed and a scanning electron microscope (SEM) procedure is used to show the successful loading photographically. The drawback of this method is that the particle size of the pigments has to be small enough that they can penetrate and be absorbed into the fiber. However, a benefit of higher optical and mechanical properties were reported compared to conventional loading methods, because filler particles are retained inside the lumen, leaving a higher surface bonding area of the individual fibers. Similar investigations on lumen loading were carried out by Miller & Paliwal nearly parallel to Middleton & Scallan with similar results [74-76].

No commercial applications of this process have been found. However, mixing the filler particles with the pulp suspension and storing this suspension in the head box feed chest, for a specific time, applies indirectly many Lumen Loading principles to today's paper making processes.

4.3 The Chemical Method:

The chemical method is not limited by pigment and particle size. This method starts with mixing and soaking the fibers in a soluble salt solution. The fiber-salt suspension is then added to another salt solution. Through chemical reactions, the pigment particles are precipitated inside the fiber pores. During research completed in China, sodium sulfate, sodium carbonate, barium chloride and calcium chloride were mixed and soaked with the fibers. Then the suspension was added into a barium chloride, calcium chloride and sodium carbonate solution. Upon examination, the barium sulfate, barium carbonate and calcium carbonate particles were found to be precipitated and present within the fiber pores [62]. The filler level increase achieved was reported between 2% and 5%, depending on the reactants used. No commercial applications of this process have been found.

Various researchers such as Chang & Chang [77-78], Maloney [79], Pantel & Mabapata [80], Roberts [81], Serth & Chan [82], and Xu & Deng [83] have discussed how paper properties are affected by Lumen Loading under low consistency operation. Results of Lumen Loading research show that both methods can provide lumen loaded fibers with up to 8% to 11% filler content for the mechanical method and 10% to 13% filler content for the chemical method. Lumen loaded handsheets have higher brightness and opacity values as well as a coarser surface structure and lower smoothness and gloss. Lumen Loading can significantly affect the strength properties of the measured handsheets, showing higher tear, tensile and bursting strength at comparable ash levels.

Most past research on PCC and GCC crystals concentrated on present industrial practices by Ahn (1996) [84], Augustin & Bohnet (1995) [85], Djarova & Kovandjeiev (1984) [86], Falini, Gazzano & Ripamonti (1994) [87], Goodarz & Motamedi (1980) [88], Hostomsky & Jones (1991) [89], Hu, Jiqiang, Yanquan & Zunxiang (1996) [60], Kamkha, Bizyaev & Sibiryankov (1989) [91], Kotaki & Tsuge (1990) [92], Kroschwitz (1993, Vol. 4 & Vol. 7) [93, 94], Laine (1980) [95], Lanjian (1998) [96], Levi, Addadi, Albeck, Brack & Weiner (1998) [97], Lindström, Silenius & Sivé (1996) [98], Matsushita et al. (1993) [99], Merris & Charles (1998) [100], Nancollas & Reddy (1971) [101-102], Pang & Gray (1998) [103], Sawada (1997) [104], Severtson, Duggirala, Carter & Reed (1998) [105], Simino (1991) [106], Shubnikov (1962) [107], Swinney, Peters & Stevens (1982) [108], Tjong & Xu (1997) [109], Yagi, Iwazawa, Matsubara & Sonobe (1984) [110]. All of the above research focused on the mass crystallization kinetics of calcium carbonate in lab scale studies. The studies simulated conventional batch crystallizer processes to explain crystallization mechanisms for seeded and unseeded operations. Kotaki & Tsuge (1990) [92], Swinney, Peters & Stevens (1982) [108], Hu, Jiqiang, Yanquan & Zunxiang (1996), Hu, Quinghua, Yanquan, Zhongwei & Zunxiang (1996) [62,90] and Laine (1998) [95], showed reaction time, initial conditions and suspension density as main contributors to the growth rate of calcium carbonate [62,90,95 107]. Godarz & Motamedi (1980) [88], studied calcium carbonate crystal growth under the microscope by merging two drops of calcium sulfate with sodium carbonate solution [50]. Hostomsky & Jones (1991) [89], studied the same process in a continuous flow crystallizer

for agglomeration of crystals [89]. They showed that crystal form is determined by the concentration of the reactant, the pH and the residence time. Kamkha, Bizyaev & Sibiryankow (1989) [91], showed that decreasing the pH increases the rate of precipitation, but does not affect precipitation of a supersaturated solution [91]. Instead, the supersaturated solution is affected by the specific surface area of the dispersion phase in the beginning of the reaction. Matsushita, et al. (1993) [99] and Ahn (1996) [84], described the calcium carbonate precipitation rate based on the ionic concentration of Ca^{2+} and OH^- ions [84,99]. Studies by Sawada (1997) [104] and Yagi, Iwazawa, Matsubara & Sonobe (1984) [110] found that the use of phosphorous-containing inhibitors increased the rate of calcium carbonate crystallization [104,110]. Merris & Charles (1998) [100] used a 6.4 liter laboratory reactor to show that PCC with high opacifying characteristics can be produced by using the causticizing reaction, also known as the Soda Ash-Lime (SAL) reaction. Reaction rates of 120 minutes to 290 minutes were reported [106]. Another aspect of precipitating calcium carbonate was discussed by Augustin & Bonet (1995) [85]. The occurrence of calcium carbonate crystallization on heat transfer surfaces is known as fouling. By adjusting the pH between 6 and 10, the fouling resistance increases due to the higher strength of the fouling layer at high pH. This strength is caused by the increasing velocity of crystal growth from supersaturation [85]. Severtson, et al. (1998) [105], described that the buildup of CaCO_3 particles in kraft digesters and black liquor evaporators is a function of temperature and having pH range of 6 to 10.5 [105].

The study of PCC has also been relevant to other fields of study. Nancollas & Reddy (1971) [101,102] discussed the calcium carbonate crystal growth during the evaporation of supersaturated solutions and its relation to geochemistry and oceanography [101-102]. Levi, Addadi, Albeck, Brack & Weiner (1998) [97] and Falini, Gazzano & Ripamonti (1993) [87] discussed precipitation of calcium carbonate in biological processes, mostly calcium carbonate containing skeletons [87,97]. These crystals were found to be structurally very similar to their inorganic counterparts (Levi, Addadi, Albeck, Brack & Weiner, 1998) [97]. Djarova & Kovandjeiev (1984) [86] discussed the occurrence of crystals in urine, the first phase of bladder stone formation [86].

Literature for evaluating calcium carbonate crystal growth has been provided by Kroschwitz (1993, Vol. 4 & Vol. 7), Laine (1980) [94-95], Lindström, Silenius & Sivéén (1998) [98]. Subkonov (1962) [107] and Tjong & Xu (1997) [109]. Pang & Gray (1998) showed the benefit of using sodium oxalate as an inhibitor for producing calcium carbonate [103] and Yagi (1994) investigated Christal growth with an chemical adsorption process [110].

4.4. The Combination Method

4.4.1. In-Situ Precipitation:

The combination of the mechanical and chemical method was first developed at the United States Department of Agriculture (USDA) Forest Products Laboratory (FPL) and further researched with focus on filler development and interaction with the paper making process by Klunghness, Claufield, Abubakr, Heise, Dölle, Sykes, Stroika, Shilts Sachs, and Tan, F. [63-67 & 111-128]. The Fiber Loading process can be described as the addition of a chemical, usually hydrated lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$), to fibrous materials. Figure 2a shows In-situ particles in the lumen and on the fiber and Figure 2b shows in situ particles in the fiber fibril network.

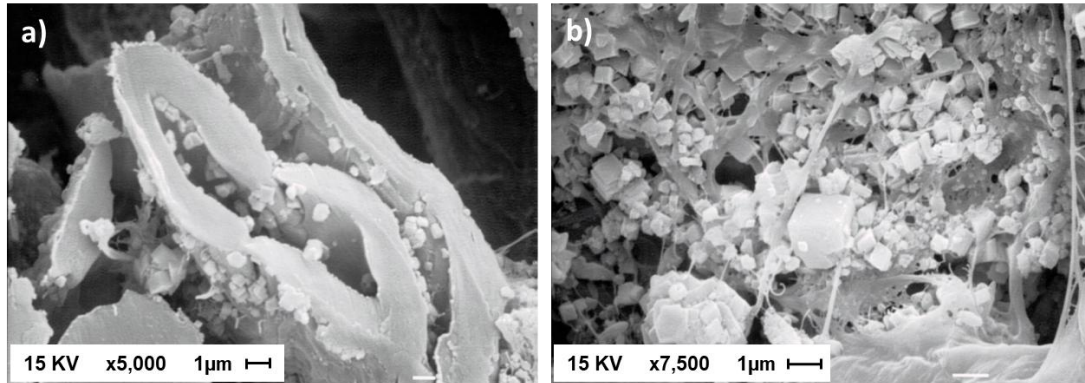


Fig. 2. a) In-situ PCC particles a) in lumen and on fiber, b) in fiber fibril network [129]

This chemical compound is added to the fibrous material at a level of up to 50%, based on the paper weight basis. The chemical compound is deposited in both, the water and the fibrous material. Carbon dioxide (CO_2) gas at a level sufficient for chemical reaction is added to the solution of the fibrous material. Under high shear mixing, the gas reacts with the slurry to form a water insoluble chemical compound, calcium carbonate (CaCO_3), precipitated on and in the fiber walls and in-between the fibers. The produced pulp slurry is then forwarded to the paper manufacturing process. The Fiber Loading process has the ability to eliminate the need for a satellite plant to manufacture PCC slurry that is normally incorporated in the pulp slurry before the head box of a paper machine [67, 112-113, 128].

It has the potential to save fibers and energy, as well as lower the waste production. In addition, carbon dioxide emissions can be reduced.

This research lead to U.S. Patent 5,223,090, RE 35,460 [63-64] and World Patent WO 92/15745t [115]. This patent describes a process in which calcium hydroxide is added to the moist pulp and then combined with carbon dioxide in a pressurized reactor to form PCC. The FLPCC is formed and then deposited both on the fiber walls and in-between the fibers [114, 125].

Voith North America Inc. conducted research on Fiber Loading on behalf of a Department of Energy, National Industrial Competitiveness through Energy, Environment and Economics (NICE³) Grant [130] with its focus on demonstrating to potential users the advantages of Fiber Loading in an industrial setting. The continual issuance of patents in present years shows that research and development efforts are still focused on the Fiber Loading technology.

At the Helsinki University of Technology, research was conducted on the precipitation of filler material to the pulp fines which are actually of the same size as the filler material itself. In addition, Fiber Loading research was performed showing the feasibility of using an aluminum compound to replace GCC. In this process, pulp fibers with approximately 15% consistency were mixed with a solution of alum. Sodium silicate and sodium hydroxide were added to the slurry by mixing over time [68].

All research on various in situ precipitation processes showed that the achieved handsheet properties have higher brightness and opacity values as well as a coarser surface structure, lower smoothness and gloss. Lumen Loading can significantly affect the strength properties of the measured handsheet, showing higher tear, tensile and bursting strength at comparable ash levels. However, no commercial applications could be found.

4.4.2. Patents Review on Paper Filler Material

Some of the first United States patents on grinding and precipitation of calcium carbonate for industrial uses were granted in the 1920's [51, 131] mostly for use as low cost paint filler and pharmaceutical agent to produce products at lower cost.

The development of PCC has led to various filing of intellectual property rights that resulted in granted patents by the United States Patent and trademark Office.

Researchers such as (Graham & Carroll (1992, 1994) [132], Green, Fox & Scallan (1985) [133], Forster & Odgen (1998) [134], Hockman (1998) [135], Hayes & Sinclair (1990) [136], Srivatsa, et. al. (1997)) [137] received patents. These patents describe a low consistency process of lumen loading, but do not give suggestions to operate a high consistency process of 20% to 25% or higher fiber content in the fibrous solution. Patents for the PCC manufacturing process are most commonly related to commercially used batch processes and equipment. Patents were granted to Baumann & Williams (1966) [138], Hall (1960) [139], Hockman (1998) [140], Irvington & Covington (1937) [141], Kogej & Smrekar (1997) [142], Matthew, Amidon, Hart & Patnaik (1997) [143], McClure (1961) [144], Miller (1961) [145], Muskat & Arkon (1940) [146], Podschus (1964, May 19 & May 24) [147], Pope & Hackley (1964) [148], Rafton (1940) [149], Schur & Levy (1953) [150], Spaepen (1999) [151], Thurner (1996) [152] and Wadsworth & Allen (1937) [153].

The patents from Baumann & Williams (1966) [138], Miller (1961) [145], Podschus (1964, May 19 & May 24) [147], Pope & Hackley (1964) [148] and Schur & Levy (1953) [150], show how precipitated calcium carbonate can be produced and used as a filler or coating medium in the paper industry. Using calcium carbonate as a pigment in paint or rubber production is taught in the patent by Muskat & Arkon (1940) [148]. However, none of these patents describes a high consistency process for production of precipitated calcium carbonate. In general, a vessel type batch reactor is used, operating under a consistency no greater than 5% of solid content in the final solution. The batch reactors used to precipitate calcium carbonate are described in the patents of Hall (1960) [139], Rafton (1940) [149] and Kogej & Smrekar (1997) [142]. With these reactors, calcium carbonate is precipitated at a consistency not greater than 5% by adding lime and CO₂ gas, while holding the temperature between 15°C and 50°C. Irvington & Covington (1937) [141] discussed a procedure to produce fine particle size calcium carbonate at approximately 55°C using limestone as the base material. The limestone is burned to release carbon dioxide and is then slaked and screened to remove impurities. The resulting slurry is passed into an agitated vessel filled with carbon dioxide gas. Hockman (1998) [135] developed a Lumen Loading process which uses common process tanks and a flocculent that binds the filler inside the lumen with a process consistency of 0.3% to 4% by weight. Spaepen (1999) [151] precipitated calcium carbonate by using calcium hydroxide as the base material and a series of static mixers where carbon dioxide is introduced. Matthews, Amidon, Hart & Patnaik (1997) [143] attached the filler directly to the fiber by keeping the fiber slurry at 5% consistency, adding CO₂ and controlling the pH of the reactants in the reactor. McClure (1961) [144] and Wadsworth & Allen (1937) [153] described a diffuser and a valve-type application to precipitate calcium carbonate during a continuous process. Thurner (1996) [152] discussed a method of continuously producing calcium carbonate by using calcium hydroxide and carbon dioxide emissions from combustion processes.

Patents related to the manufacturing process of calcium carbonate crystals at a consistency of 5% or less, were granted to the following researchers: Arika, Mitari, Takitani & Yamamoto (1979) [154], Bleakley & Jones (1993) [155], Birchall (1971) [156], Chapnerkar & Badgujar (1994) [157], Ebinuma, Saitho, Sakaguchi & Yokoj (1990) [158], Marthur, Resnik & Simmons (1990) [159], Marthur & Resnik (1990) [160], Merris (1994) [161], Brooks & Rafton (1936) [162], Takeshi, Matsukawa & Tanaka (1991) [163], Vanderheiden (1987) [164] and Waldeck (1967) [165]. These patents focus on the manufacture of calcium carbonate crystals in their various forms. Waldeck (1967) [165] and Arika, Matari, Taktani & Yamamoto (1979) [154] discussed chain-structured crystals. Needle-shaped crystals were explained by Birchall (1971) [156]. Vanderheiden (1987) focused on spherically shaped crystals [164], while palette-shaped crystals have been discussed by Takeshi, Matsukawa & Tanaka (1991) [163]. Bleakley & Jones (1993) received a U.S. patent for cluster-shaped scalenohedral crystals [155]. Scalenohedral and rosette-shaped crystal manufacturing processes were

patented by Merris (1994) [161]. Chapnerkar & Badgujar (1994) discovered the manufacturing process for rhombic and barrel shaped crystals [157]. Large surface area and finely divided calcium carbonate crystals were investigated by Mathur, Resnik & Simmon (1990) and Marthur & Resnik (1990) [159, 160]. Colloidal calcium carbonate production was patented by Rafton (1936) [149]. The manufacture of colored precipitated calcium carbonate was developed by Ebinuma, Saitho, Sakaguchi & Yokoj (1992) [158].

Implementation of these precipitation processes into the papermaking process is demonstrated in patents granted to the following researchers: Cousin & Mora (1998) [166], Craig (1948) [167], Forster & Odgen (1998) [134], Shannon (1999) [168], Shibazaki, Edagawa, Hasegawa & Kondo (1979) [169], Sillenlus (1997) [170] and Thomson (1962) [171].

The processes of Cousin & Mora (1998) [172] introduced calcium carbonate of sizes 0.5 to 10 microns onto the fibers, while Craig (1948, 1952) [167,173] described a process where pigmented pulp is produced using commercial waste calcium chloride liquor. In this process, the calcium chloride is attached around and between the fibers. Forster & Odgen (1998) [134], improved the optical properties by using a soluble, optically active dye in the Lumen Loading process for hygienic end use paper. Sillenlus in an European patent application (1997) described a procedure for adding filler into a pulp based cellulose fiber by stirring the fiber suspension at a consistency between 5% and 18% while adding the filler [170]. Shannon (1999) discovered a loading process for metal dioxides by absorbing an organometallic compound into the fiber walls [168]. In this process the fibers are dry slurried with a non-aqueous solvent and thereafter contacted with water to precipitate the metal oxides or metal hydroxides to achieve better optical and paper properties. Shibazaki, Edagawa, Hasegawa & Kondo (1979) described a process with 0.1 to 5% consistency that added both calcium hydroxide and carbon dioxide to precipitate calcium carbonate between 15°C and 80°C [169]. Thomsen (1962) discussed the precipitation of calcium carbonate in a solution of 5% to 29%. He used a chloride selected from the group of calcium and magnesium to improve the opacity of the paper sheet [171].

A high consistency lumen loading process that precipitates Calcium carbonate particles at high consistencies between 5% to 60% % was investigated by FPL and patented in 1993 and 1997 [67-68]. Further patents were granted to Dölle, Heise, Lorenz, Matz, Rheims, Sigl Witek [174-188] for processes of manufacturing PCC attached to the inside and outside of cellulosic fiber surfaces using unpressurized and pressurized reactor combination at solids contents of up to 70%.

5. CONCLUSION

Since the invention of the paper by in 105 CE to Chai Lun many improvements have been made to the paper product we know today. Paper was a handmade product till the late 1800's and beginning 1900's when Nicolas Louis Robert and Henry and Sealy Fourdrinier invented continuous paper manufacturing machines. Today's machines can be over 600 m long and 11.5 m wide, running at speeds of over 2000 m/min, and producing up to 4,500 metric tons per hour. Paper as we know it today, can be characterized as an orthotropic thin plate with a thickness of over 500 μm and a basis weight of over 500 g/m^2 depending on the manufactured paper products unique requirements.

Today many different additives are used to achieve the required paper properties. The major used additive to enhance optical paper properties and save fiber material at the same time are calcium carbonate based filler materials, which have approximately 70% market share in North America, and can be added to a maximum of 20 to 25% based on fiber material. Prior to the 1980's ground calcium carbonate based filler materials were added. In the 1970's a shift from acid to neutral papermaking started which made it possible to use precipitated calcium carbonate in the paper manufacturing process.

The enhancement of printing technologies required paper with superior properties for printing, which led to an increase in filler content and specially designed filler particles. The in-situ precipitation and filler manufacturing processes known today, can be divided into a mechanical method, a chemical method and a combination of the mechanical and chemical method.

The mechanical method uses high shear and centrifugal forces to load the fiber pores with the filler particle.

The chemical method precipitated the pigment particles in a solution. A solution containing the filler particles is added to the paper making process. This is the common method in producing precipitated calcium carbonate since the 1980's.

The combination method utilizes the mechanical and chemical method in precipitating the calcium carbonate particles in the presence of fiber material.

All research on various in situ precipitation processes since the 1970's showed that the achieved handsheet properties have higher brightness and opacity values as well as a coarser surface structure, lower smoothness and gloss. In-Situ processes showed improvements for the paper manufacturing process in regards to physical and mechanical handsheet paper properties.

However, no commercial applications of this process have been found at present time. However, mixing the filler particles with the pulp suspension and storing this suspension in the head box feed chest, for a specific time, applies indirectly in-situ principles in today's paper making process operations.

6. COMPETING INTERESTS DISCLAIMER:

Author has declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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