

# Fillers for Papermaking: A Review of their Properties, Usage Practices, and their Mechanistic Role

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Issues of cost and product quality have caused papermakers to place increased attention on the use of mineral additives, which are the subject of this review article. Technologists responsible for the production of paper can choose from a broad range of natural and synthetic mineral products, each of which has different characteristic shapes, size distributions, and surface chemical behavior. This article considers methods of characterization, and then discusses the distinguishing features of widely available filler products. The mechanisms by which fillers affect different paper properties is reviewed, as well as procedures for handling fillers in the paper mill and retaining them in the paper. Optical properties of paper and strategies to maintain paper strength at higher filler levels are considered. The goal of this review is to provide background both for engineers working to make their paper products more competitive and for researchers aiming to achieve effects beyond the current state of the art.

*Keywords:* Fillers; Minerals products; Calcium carbonate; PCC; Kaolin clay; Titanium dioxide

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## INTRODUCTION

Fillers, the subject of this review article, can be defined as water-insoluble, particulate substances in the size range of about 0.1 to 10  $\mu\text{m}$  that are added to slurries of cellulosic fibers before the formation of paper. In terms of the amounts used, fillers rank second only to fibers themselves as an ingredient of paper. In addition to having a huge economic impact, fillers also provide a fascinating field for scientific and technological investigation. This review article considers the subject of fillers in general, emphasizing the results of past research work related to this subject.

The job of summarizing the subject of fillers would be more difficult, except for the existence of previous review articles and book chapters. In particular, it is important to acknowledge the following review articles and book chapters (Anon. 1958; Schwalbe 1962; Morris and Brooks 1973; Solomon and Hawthorne 1983; Koppelman 1984; Gill and Hagemeyer 1992; Scott 1996; Keegan 1999; Wypych 1999; Shen *et al.* 2009b).

## Main Classes of Fillers for Papermaking

The most widely used fillers for papermaking can be described as inorganic, particulate materials. As shown in Table 1, it is possible to divide these materials into two main classes, natural and synthetic. Some minerals, such as calcium carbonate, are

available as fillers in both natural and synthetic forms. Other minerals, such as talc and titanium dioxide, are mainly restricted to either the natural or the synthetic category of fillers, respectively.

**Table 1.** Classification of Major Papermaking Fillers as either Natural or Synthetic

Mineral Composition	Natural Products	Synthetic Products
CaCO <sub>3</sub>	Ground limestone (GCC)	Precipitated calcium carbonate (PCC)
	Chalk (ground)	
Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O	Clay (hydrous kaolinite)	Precipitated aluminum silicate
TiO <sub>2</sub>	-	Titanium dioxide (rutile and anatase forms)
Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Talc	-
CaSO <sub>4</sub> ·2H <sub>2</sub> O	-	Gypsum

Worldwide, papermakers are using at least 6 to 8 million metric tons per year of minerals for filling and coating (Mackie and MacKenzie 1999). Other estimates can be higher. According to Chamberlain and Kirwan (2014), mineral products for wet-end addition and coatings make up 8% of the materials used in the paper industry. Those authors do not specify whether they are excluding ordinarily unfilled grades of paper such as linerboard and tissue; however, if one combines the 8% figure with a world production of 403 million metric tons of paper and paperboard production in 2013 (RISI 2014), one can calculate about 32 million metric tons of mineral per year in the world as a high estimate. CEPI (2013) has estimated a proportion of about 14.6% non-fibrous content of paper products made in Europe. Based on further information provided by CEPI, the average amount of calcium carbonate in European can be estimated as 8.4% and the average amount of kaolin products can be estimated as 3.2% relative to the mass of paper and paperboard.

In North America over 2 million tons involve production of precipitated calcium carbonate (PCC) (Anon. 1999), and paper filling is by far the major use of PCC. An exact ratio between mineral usage for filling vs. coating is often hard to determine, since many mineral products can be used in either application. Furthermore, coating materials present in recovered fibers or in broke (internal recycling) are likely to become part of the net filler content of paper products.

The mineral content of paper differs markedly by grade (Auhorn 2009). Some grades of paper, such as tissue and milk carton board, often contain little or no filler. By contrast, printing papers often include between 5 and 30 percent of filler by mass. Uncoated, supercalendered grades of paper often contain even higher levels. In the distant past, little to no filler has been used in such paper grades as newsprint and bleached paperboard, but that situation has been changing (Burke 1993; Ain and Laleg 1997).

For several reasons, the percentage of filler used in a given grade of paper has gradually increased over time (Breunig 1981; Weigl and Ritter 1995). It is easy to understand such trends in cases where the delivered cost of fillers is less than that of the fibers. In other cases, fillers make it possible for the papermaker to meet customer requirements for opacity or brightness at lower net cost. It even makes sense to describe

papermakers' use of fillers as an addiction; though papermakers occasionally reduce the level of filler, they seldom "kick the habit" once they begin using filler in a given product.

Starting in the 1960s in Europe, there has been a strong trend in the direction of calcium carbonate fillers. Because the presence of calcium carbonate generally causes the pH of a papermaking system to remain above a value of 7, the term "alkaline papermaking" has been used. In the United States the most dramatic shift in the composition of paper occurred during the late 1980s and 1990s. Printing papers made before that period mostly contained clay fillers. By the end of that period, precipitated calcium carbonate accounted for more than 80% of the filler used in such paper (Gill and Haskins 2000). Factors that motivated the shift from clay to calcium carbonate included the cost of achieving brightness and opacity (Gill and Hagemeyer 1992; Burke 1993). As alkaline papermaking has emerged as the dominant practice for printing paper production, it has been necessary to transform the type of chemicals used for paper manufacture, especially in the case of internal sizing agents used to make paper resist fluid penetration (Dumas 1981; Hodgson 1994). The higher extract pH of paper made under alkaline papermaking conditions has had a favorable side benefit, a much slower deterioration of strength properties upon storage, compared to paper made under acidic conditions with aluminum sulfate (Hubbe 2005b; Zervos 2010).

Clay and titanium dioxide continue to be widely used as fillers. Talc, gypsum, aluminum trihydrate, and synthetic silicates and silica products also have various applications as fillers, depending on the grade of paper being made, and also the regional availability of different mineral products.

### **Fillers Don't Just "Fill"**

Despite their somewhat humble name, fillers do much more than just occupy space within paper. Fillers affect paper's structure, appearance, and many measurable properties that determine paper's end-use performance in different applications. If one "fills a hole," one adds something to occupy an existing void volume. But in the case of papermaking, what we call fillers are added before the structure of paper yet exists. As will be discussed, because of the way paper is formed, fillers can profoundly affect the thickness of the resulting product. By partly interrupting the bonded area between fibers, most fillers tend to decrease the strength properties of paper. In some cases filler use increases the fraction of void volume of paper, especially if the caliper is measured before the paper is calendered (Bown 1983). The proportion and dimensions of empty spaces within the sheet have a large impact on optical properties, in addition to the paper's permeability and interaction with inks.

Most papermaking fillers have maximum dimensions in the range of about 0.2 to 4  $\mu\text{m}$ . To put this size range into perspective, the diameter of a typical filler particle is only about 1/1000 of the length of a typical papermaking fiber, which usually is about 1 to 3 mm. Though it is possible to see individual filler particles under a high-power optical microscope, their presence is more often made apparent by indirect tests, including ash analysis of paper samples, measurements of paper properties, and the light scattering characteristics of mineral suspensions. Because typical papermaking fillers are so small, their retention during the paper forming process presents technical challenges, and these will be considered later in this article.

## Main Benefits of Filler Use

As summarized in Table 2, there are a variety of benefits that papermakers and their customers can derive from the use of fillers in paper (Schwalbe 1962; Kapoor *et al.* 1996). While not all of these benefits may be important for a particular type of paper, fillers offer the manufacturer of paper products a variety of ways to meet customer needs and improve profitability. Depending on the type of paper being made, the product attributes most likely to benefit the most from filler use are brightness, opacity, smoothness, dimensional stability, print quality, and the overall cost of materials (Brecht and Pfretzschner 1936; Schwalbe 1962; Morris and Brooks 1973; Gill and Hagemeyer 1992; Scott 1996). The selection of what type of filler to use, and also the amounts added, will depend on which of these attributes are critical to the paper's end use, and in what proportions.

**Table 2.** Benefits of Filler Use in Paper

Benefits of Filler Use	Ways to Maximize the Benefits	Citations
Cost reduction	Increased filler content, using low-cost fillers	Davidson 1965
Brightness	Increased filler content, using bright fillers	Bauch 1992
Opacity	Increased filler content, especially using fillers with optimum size of the primary particles. Best results with high refractive index filler	Bown 1998
Reduced energy of drying the paper	Increased filler content	Kapoor <i>et al.</i> 1996
Friction – to <i>increase</i> the paper-to-paper coefficient	Composite structure of filler, e.g. calcined clay, scalenohedral PCC	Rooks 1993
Friction – to <i>decrease</i> the paper-to-paper coefficient	Platy filler with easy delamination, e.g. talc	Biza 1999
Control of pore size, e.g. for filter papers	Selection of size and particle shape of filler	Schwalbe 1962
Controlled burn rate, e.g. for cigarette paper	Use of aluminum trihydrate (ATH)	Schwalbe 1962

Fillers have played an especially prominent role in the manufacture of paper products intended for printing. Although bleached kraft fibers have achieved a position of dominance for high-end printing papers, the fibers themselves do not contribute sufficient interaction with light to meet customer requirements for opacity in typical grades of printing papers. The translucent nature of paper made from bleached kraft fibers only tends to increase when the papermaker applies mechanical action to the fibers, *i.e.* refining, to enhance inter-fiber bonding and increase the apparent density of the paper (El-Hosseiny and Abson 1979; Young 1980). Filler usage has allowed producers of printing papers to meet their customer's needs for opacity at lower overall values of basis weight, *i.e.* the mass per unit area of their product.

So-called “wood-containing” paper products, which contain thermomechanical pulp (TMP) or groundwood also have benefited from filler use, especially with respect to brightness, smoothness, gloss (in supercalendered grades), and resistance to strike-through or show-through of print (Weigl and Ritter 1995). More recently there has been a trend

towards calcium carbonate use in wood-containing papers (Burke 1993; Ain and Laleg 1997), despite the fact that high-pH conditions tend to darken lignin-rich fibers (Poirier *et al.* 1996; Varhimo *et al.* 2013). Varhimo *et al.* (2013) found evidence that such brightness reduction could be due to precipitation of certain dissolved and colloidal chromophoric species onto calcium carbonate. Innovative strategies to be able to use calcium carbonate fillers at lower pH (Tokarz *et al.* 1990; Mathur and Lasmarias 1991; Passaretti *et al.* 1993; Patel and Panigrahy 1996a,b; Ain and Laleg 1997; Pang *et al.* 1998, 2003) will be discussed later.

Filler's effects on optical characteristics of paper generally can be understood in terms of well-known principles of light scattering and absorption (Bøhmer 1981; Middleton *et al.* 1994). On the one hand, the particle size of most filler materials is not much larger than the wavelengths of visible light. Because of this fact, fillers can have a relatively high efficiency of diffusely scattering much of that light back in the direction of the user. On the other hand, filler particles can act as spacers in the paper sheet, increasing the frequency of void spaces between cellulosic material. Such inter-fiber spaces usually account for a major part of the benefit, in terms of paper brightness and opacity (Bown 1985a). Because of this relationship between paper structure and its optical properties, it will be important to consider the effects of different particle shapes and sizes of the available materials that can be used as fillers (Hubbe 2004).

In addition to affecting brightness and opacity, fillers also can change the relationship between thickness (caliper) and smoothness of a paper product. It is easy to understand that replacement of some of the fiber mass by much smaller particulate material can result in a smoother product. What is less obvious is the fact that different kinds of fillers can either densify or increase the bulk of a paper sheet, especially when the effects are considered before the paper is subjected to a calendering operation (Gill 1989). Fillers that tend to contribute more caliper to the paper, at a given basis weight, allow the papermaker to apply more intense calendering, and such practices typically result in a greater degree of smoothness (Gron and Ahlroos 1998; Gill *et al.* 2003; Laufmann 2005). Alternatively, papermakers can use types of fillers that pack together efficiently during the papermaking process, resulting in relatively dense paper. High paper density sometimes can benefit such paper properties as tensile strength and resistance to air permeation, depending on the needs of the user.

Though the delivered cost of filler materials is often lower than that of fibers, it is important to keep in mind that the paper needs to meet certain requirements of the end user. Thus, the final cost of the product has to include not only the filler, but also any changes in refining, starch use, and other chemicals that are required in order to compensate for the loss in inter-fiber bonding strength that occurs with addition of fillers. Because most fillers are very small, and their surfaces are rigid, *i.e.* not pliable, they cannot provide the same contribution to paper strength as cellulosic fibers. In addition to strength, the papermaker also needs to consider the impact of filler use, including the amount of mineral added to paper, on the efficiency of paper machine and converting operations. In short, the benefits of filler use need to be sufficient to justify their full effect on the cost of a product that meets the customer's needs.

Additional benefits of filler use are discussed in subsequent sections. Many of these benefits are related to surface properties of paper. Indeed, one of the main things that

papermakers contribute to their customers is a surface. The paper surface can provide means of communication, barrier properties, tactile properties, and support. Because the surface area of a typical filler product, per unit mass, is of the order of magnitude ten times higher than that of typical dry papermaking fibers, the filler can contribute a high proportion of the surface of a typical paper sheet. If a given type of filler has a beneficial interaction with inks, glues, or plastic laminates applied to the surface of the paper, this can be an important advantage in terms of paper product differentiation. Once again, some understanding of the composition and morphology of common filler varieties can be helpful when the papermaker considers the most advantageous uses of these materials.

### Key Problems Associated with Filler Use

As shown in Table 3, some common effects of using fillers are generally regarded as unfavorable. However, as indicated by the entries in the second column of the table, suppliers and users of papermaking fillers have developed various ways to minimize various undesired effects.

**Table 3.** Problems Associated with Filler Use

Filler-Related Problem	Strategy to Minimize Problem	Citations
Strength decrease, higher frequency of web breaks	Larger particle sizes, cationic starch, increased pulp refining	Bown 1985b
Increased apparent density of the paper	Use of bulky fillers, fiber optimization	Moberg 1985a,b
Low first-pass retention, two-sidedness of paper sheet	Effective retention aid use	Tanaka <i>et al.</i> 1982
Abrasion of forming fabrics, slitter knives, die cutters	Avoidance of quartz impurities, fine particle size	Laufmann and Rapp 1995
Dusting, contamination of printing presses, copiers	Surface-applied starch	Fineman and Hoc 1978
Increased demand for sizing agents, <i>etc.</i>	Increased chemical dosages, reduced filler content, larger particle size	Krogerus 1999; Chabot <i>et al.</i> 2004

With respect to strength issues, it makes sense that when you replace load-bearing fibers with small, granular material, one can expect a reduction in strength of the resulting paper (Bown 1998). As will be described in more detail later in this chapter, fillers tend to interrupt the formation of inter-fiber bonds in paper. It is often possible to compensate by increased refining and/or by increasing the amount of dry-strength additives, such as cationic starch at the wet end of the paper machine and surface-applied starch solutions. However, strength issues provide limits to filler levels that can be practically achieved in various paper grades, depending on the fiber furnish, as well as the papermaking equipment being used.

### FILLER CHARACTERIZATION METHODS

Methods for characterizing filler materials have been reviewed by others (Huber 1967; Gill and Hagemeyer 1992; Wypych 1999). The methods generally fall into three

categories: (a) tests related to filler product specifications; (b) tests that can be helpful with respect to troubleshooting and product development efforts; and (c) online process control tests.

### **Mineral Characteristics**

Some of the most important characteristics of fillers can be anticipated from the composition and crystalline nature of the materials. Though papermakers themselves seldom carry out the analyses needed to determine filler's composition or crystalline nature, knowledge of these factors can be helpful in making decisions regarding filler use. For instance, it may be possible for the supplier of the filler material to substitute a different grade of mineral that better meets the papermaker's needs. In other cases, the process of preparing the minerals may be adjusted to avoid some of the problems summarized in the previous section. In yet other cases the papermakers can choose among several different potential filler materials in order to meet customer objectives at minimum cost.

#### *Hardness*

Hardness of papermaking fillers is usually reported on the Moh's scale, a rating system derived from pair-wise tests to see which material will scratch the other. Talc, if it is pure, has a very low Moh's hardness value of 1 (Biza 1999). By contrast, calcite, the most important mineral form of  $\text{CaCO}_3$ , has a hardness of 2.9 to 3.0 (Hagemeyer 1984), and titanium dioxide has a hardness of 5 to 7, depending on the crystal type (Wypych 1999). Kaolin has a Moh's hardness of about 2. Of course, all of these cited values are useful only if the material in question is relatively pure and properly labeled. As will be noted later, fillers can be highly abrasive if they contain a significant amount of quartz impurity, which has a crystalline hardness of 7 (Wypych 1999).

#### *Refractive index*

Refractive index is a measure of a material's ability to bend light as it passes through an interface. Most papermaking fillers have refractive index values within the relatively narrow range of about 1.5 to 1.65. Because cellulosic fibers have approximately the same refractive index, light will not bend or scatter to a significant degree when it passes directly between a fiber surface and an immediately adjacent particle of filler. The most important exception to this rule is titanium dioxide. The rutile and anatase forms of  $\text{TiO}_2$  have refractive index values of 2.7 and 2.55, respectively. The high contrast between  $\text{TiO}_2$ 's refractive index and other components of paper make this mineral especially effective for increasing paper's opacity, even in cases where the paper is so dense or filled with wax that few air spaces remain in the product.

#### *Solubility*

Solubility varies considerably among different types of mineral products, ranging from highly insoluble materials such as  $\text{TiO}_2$ , to gypsum (calcium sulfate dihydrate), which has a solubility of about 2 to 4 grams per liter under papermaking conditions (Hofmann *et al.* 1990). The solubility of a given type of filler can depend on such factors as temperature, pH, and the concentrations of ions that are involved in chemical equilibria of the materials in question. For example, ordinary calcium carbonate becomes soluble when the pH is

reduced below about 6.5. Though it is often assumed that solubility is determined by the composition of the mineral, in addition to the temperature and solution characteristics, it is important to bear in mind that imperfect crystals and amorphous inorganic materials sometimes have considerably greater solubility, compared to tabulated values (Hancock and Parks 2000; Raz *et al.* 2002; Neck *et al.* 2003). At the other extreme, calcium carbonate is sometimes treated in order to reduce its solubility under weakly acidic conditions (Pang *et al.* 2003). Likewise, Feng *et al.* (2015) showed that the solubility of calcium sulfate whiskers could be reduced by treating their surfaces with sodium hexametaphosphate and silica.

#### *Wettability*

The free-energy attributes of the surface of a filler product can be useful information for dealing with problems related to wetting and dispersing of the dry filler, pitch absorption by filler particle in a slurry, and adhesion phenomena, including bonding of the filler particles within the paper. As noted by Huber and Weigl (1972), there can be huge differences in this quantity, depending on such factors as mineral composition, crystal faces, imperfections in the crystal, and impurities coming from the solution. Talc, which is well known for its oil-loving and pitch-loving surface, has a reported surface free-energy of  $31.5 \text{ mNm}^{-1}$  (Giese *et al.* 1991), which is lower than that of water,  $72 \text{ mNm}^{-1}$ . By contrast, pure kaolinite and titanium surfaces can have energies in the range of 500 to 700  $\text{mNm}^{-1}$  (Huber and Weigl 1972), which is about a factor of ten higher than water's surface tension. Water quickly spreads on such high-energy surfaces in cases where they are not already covered by low-energy materials, such as waxes or oils.

#### *Crystal structure*

The crystal structure of a mineral product can be deduced from X-ray refraction tests, in combination with the extensive theory of crystal types and cleavage planes (Fang 1977). While the crystalline identity of filler materials purchased by papermakers is seldom in question, such tests can be useful for determining purity, identifying the origin of various deposits on papermaking equipment, and in certain analyses to determine the composition of paper products (Delgado and Gomes 1995).

### **Filler Properties Controlled by the Supplier**

In contrast to the properties just mentioned, various other characteristics of fillers can be influenced to a large extent by the supplier. Some of the most important of these properties, from the standpoint of the papermaker, are as follows:

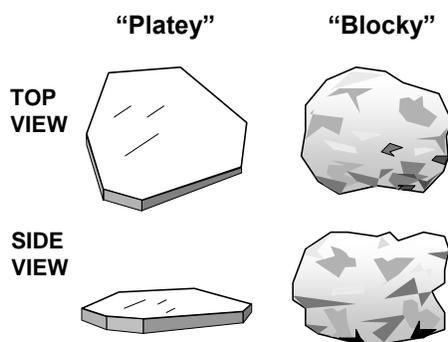
#### *Brightness*

Brightness is not entirely inherent in the crystalline nature of a papermaking filler. Rather, brightness depends on such factors as particle size and the amount of pressure applied to densify the material before the brightness measurement is carried out. In principle, one measures the fraction of incident light that is reflected diffusely from the surface of a packed bed of dry filler (Wypych 1999). Though such information can be helpful, in a relative sense, when it comes to selecting filler materials, it is important to point out that there may be only an indirect relationship between filler brightness and paper

brightness. As will be discussed later, much of the effect of fillers on paper optical properties, including opacity, is due to the interruption of bonded areas between adjacent fibers. It is worth noting that impurities account for much of the difference between “pure white” and the actual measured brightness of a typical filler product.

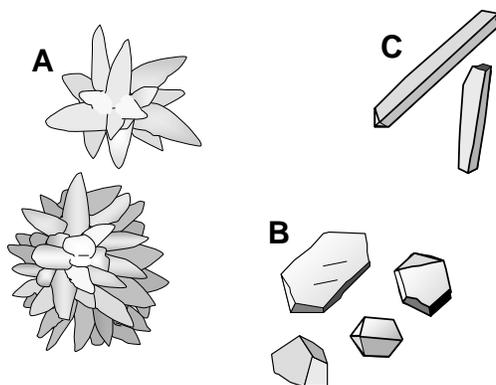
#### *Determination of filler particle shape*

With the development of scanning electron microscopy (de Silveira *et al.* 1995), papermakers have become much more aware of the differences in characteristic shapes between different types of filler materials. As illustrated in Fig. 1, many filler products can be classified as being either “platy” or “blocky” in shape. Representatives of the “platy” category of materials used as fillers for paper include not only clay (kaolinite), but also talc and mica. Ground calcium carbonate (limestone) is one of the most widely used filler materials having a blocky shape.



**Fig. 1.** Particle shape, a critical attribute of papermaking fillers

Figure 2 illustrates a few of the particle shapes that are characteristic of different types of precipitated calcium carbonate (PCC) fillers (Gill 1989). The particles at left are often called “rosettes,” and they are composed of fused clusters of the scalenohedral form of calcite  $\text{CaCO}_3$  crystals. However, by varying process conditions during PCC production (see later), it is possible to produce the other shape categories shown, including blocky, rice-like, and needle-like (acicular) forms of PCC.



**Fig. 2.** Idealized shapes of precipitated calcium carbonate particles. A: scalenohedral (rosette); B: rhombohedral; C: acicular

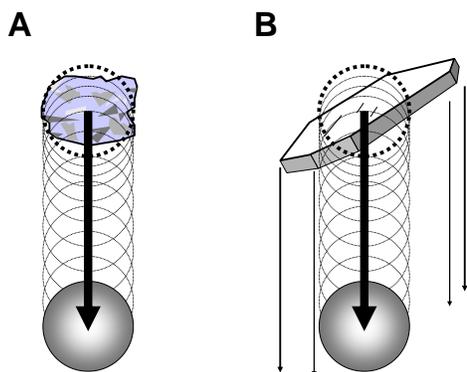
Because most microscopic methods produce two-dimensional images, it has been a continual challenge to obtain reliable information about particle shape, especially in the case of platy particles. As noted already, sedimentation tests of thin, platy fillers give results that appear to under-estimate the size, compared to microscopic images. As noted by Slepetyts and Cleland (1993), it is possible to estimate particle thickness by measuring the lengths of shadows cast by sputter-coating of SEM substrates applied at a high angle.

Jennings (1993) showed that it was possible, in principle, to obtain both size and length-to-thickness ratio information by using a combination of sedimentation and light scattering data. Beckett *et al.* (1997) and Lohmander (2000) estimated the aspect ratios of several clay samples using this kind of approach.

### Particle size

The mean particle size and size distribution can be determined by a variety of direct and indirect methods. SEM imaging probably can be considered as a benchmark method, against which other methods are judged (de Silveira *et al.* 1995).

In industrial practice it is convenient to express particle size as an “equivalent spherical diameter,” making it possible to deal with a variety of particle shapes. In principle, the concept of “equivalent spherical diameter” can be applied to data based on sedimentation, surface area determination, or projected area in microscopic images (Obbink 1977). Of these three possibilities, sedimentation rate determinations have become the most widely used in industry. As reviewed by Zeidan *et al.* (2003), the common method based on sedimentation involves centrifugation of a slurry. As illustrated in Fig. 3, in the case of a blocky particle, the equivalent spherical diameter based on sedimentation may approximately equal the diameter estimated from micrographs.



**Fig. 3.** Illustration of particles having contrasting shapes similar equivalent spherical diameters

By contrast, in the case of highly platy particles, the equivalent spherical diameter based on sedimentation is likely to be much smaller, compared to the projected area estimated from microscopy. Thus, particle size determinations based on the equivalent sphere concept can give misleading results in cases where the particles are decidedly non-spherical or composed of primary particles fused together. In the case of the most widely used fillers, results of sedimentation tests are often expressed as the “percent smaller than

2  $\mu\text{m}$ ,” based on an equivalent sphere having the same density as the mineral being evaluated. As noted by Bown (1996), filler agglomeration processes often produce structures that can be approximated as spheres; however the effective density of those spheres may not be known accurately.

For particles having a relatively narrow size distribution, especially if the particles are smaller than about 300 nm (or 0.3  $\mu\text{m}$ ), the photon correlation spectrometry method is recommended (Filella *et al.* 1997). The principle of the measurement is auto-correlation of light signals coming from fields of particles that are undergoing Brownian motion. In other words, the thermal kinetic energy of the system causes the suspended particles to ceaselessly move around in a jerky, random manner. Sequential signals coming from the scattered light can be correlated to each other if the data are collected very close in time, but the correlations become weaker with the passage of time. Since smaller particles have higher average Brownian diffusion rates, it is possible to fit the results to various assumed distributions of particles, *e.g.* a log-normal distribution. Results depend on knowledge of the refractive index, and, again, all particles are treated as if they are equivalent spheres.

#### *Filler content in paper*

The filler content is most commonly determined by incineration of a known mass of paper (Kocman and Bruno 1996; Anon. 1997). Such procedures result in vaporization of the entire organic content of the paper. In order to obtain reliable results it is essential that the conditions of temperature, time, and various other procedural details be followed faithfully. With a few exceptions, such as  $\text{TiO}_2$  and calcined clay, most commonly used mineral fillers lose a significant fraction of their original mass when incinerated under typical conditions used by papermakers.

In cases where quantitative analysis is the goal, a high furnace temperature, such as 900  $^{\circ}\text{C}$ , is often recommended (Anon. 1997). Under sufficiently vigorous heating conditions minerals such as calcium carbonate and clay can be expected to complete their chemical transformations, resulting in the release of gaseous byproducts such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . By knowing the loss-on-ignition of the filler material present in the paper, it is then possible, in many cases, to back-calculate the amount of filler that was originally present in a given mass of the paper. Because the loss on ignition is not the same for different fillers, quantitative determination of filler content in paper that contains more than one kind of mineral require a more detailed analysis. For example, it is possible to carry out an X-ray fluorescence analysis of the ash and use the results to deduce the ratios of two or more fillers that are assumed to be present in the paper.

For purposes of process control the repeatability of ash determinations often is more important than quantitative accuracy. One practical approach has been to employ relatively low-temperature ashing conditions (Kocman and Bruno 1996). An ashing temperature of about 400  $^{\circ}\text{C}$  is expected to leave most of the fillers in their original chemical form, so that no loss-on-ignition needs to be considered for determination of the filler. The downside to this technique is the relatively long time to process such a sample.

A rapid method for ashing of paper involves burning a small sample in a stream of oxygen gas (Anon. 1980). The sample is held in a screen basket made of platinum. Such tests use the burning process itself in order to achieve the desired range of temperatures needed to complete the off-gassing of the minerals. Since combustion takes place in a few

seconds, there is less delay in obtaining off-line information that may be used for process control.

#### *X-ray diffraction for type and content of filler*

As an alternative to ashing of paper, X-ray diffraction measurements can be used to quantify filler levels (Delgado and Gomes 1995). The analysis takes advantage of the crystalline regions in the cellulosic component of the paper. The intensity of the diffraction signals corresponding to crystalline cellulose can be compared to spectral features associated with one or more kinds of filler.

#### *Abrasion*

The abrasive nature of filler materials can cause problems both during and after the formation of paper. For example, the use of certain calcium carbonate, titanium dioxide, and calcined clay as fillers have been correlated to more rapid wear of forming fabrics (Chang and Henderson 1987; Schlegel and Kilpeläinen 1995; Laufman and Rapp 1995; Heger 1998). Abrasion generally has been found to increase with increasing particle size of the filler, and also with the presence of hard, crystalline materials, including quartz.

Abrasion problems on the paper machine can be minimized by careful selection or timely replacement of hydrofoil surfaces and rubbing surfaces of vacuum boxes on the paper machine (Kilpeläinen and Schlegel 1997). It appears that coarse filler particles can become lodged in small fissures in the stationary elements over which the forming fabric travels, causing an effect similar to that of sandpaper. In the paper product, abrasive fillers can cause rapid dulling of cutting elements and abrade the printing blanket surface of an offset press (Smaine 1985).

The Einleiner test is the best known method for comparing the abrasiveness of different mineral products when they are in slurry form (Chang and Henderson 1987; Schlegel and Kilpeläinen 1995; Heger 1998). To run this type of test, a sample of forming fabric is placed in a vessel with 100 g of mineral in 1000 g of aqueous solution. The fabric is then rubbed against a ceramic rotor under specified conditions. Results are sometimes expressed as the fractional width of a strand of the forming fabric that is worn away under specified conditions (Heger 1998).

To estimate the abrasivity of paper, especially if there is a concern about the rate of wear of slitter knives or converting equipment, it is possible to run a “needle abrasion test.” Such tests use a sewing machine, equipped with soft needles that are pressed a defined number of times through a specified number of paper sheets (Kurrle 1980).

## **NATURAL, MINED FILLER PRODUCTS**

The word “mineral” can serve as a reminder that essentially all inorganic materials used by papermakers are available as a result of mining. In addition, it can be useful to use the term “natural” to refer to those materials that remain as solids between the time of their removal from the ground and their delivery to the customer. Thus, the category of natural mined fillers will be taken to include products that may be ground, fractionated, purified, or exposed to very high temperatures in a furnace (calcined), as long as their form and

chemical nature remains closely related to the starting material. By contrast, precipitated or “synthetic” minerals are formed from various solutions, as will be discussed later.

While most mining operations can be described, roughly, as “digging holes in the ground and collecting what you dig up,” there can be considerable differences in these operations depending on the type of mineral, as well as local geological differences. Some of the most important papermaking filler materials obtained directly from mining include the ground limestone and chalk forms of calcium carbonate, kaolin clay, and talc. Table 4 summarizes typical properties of these four types of filler (Schwalbe 1962; Gill and Hagemeyer 1983; Gill 1991; Wypych 1999). It is worth noting that all of these naturally-derived filler products have similar densities and refractive indices. On the other hand, there are some characteristic differences in particle shape, aspect ratio, and typical brightness levels.

**Table 4.** Summary of Typical Properties of Four Major Papermaking Fillers Derived from Natural, Mined Materials

Product Type	Clay (kaolin)	GCC (limestone)	Chalk	Talc
Density (g/cm <sup>3</sup> )	2.6	2.7 to 2.9	2.7 to 2.9	2.7 to 2.85
Hardness (Moh's scale)	2	3 to 4	3 to 4	1 to 1.5
Loss on ignition, 900 °C (%)	12 to 14	43.5	43.5	4.8 to 17
Refractive index	1.55	1.48, 1.65, 1.7	1.48, 1.65, 1.7	1.58
Mean diameter (µm)	2 to 5	0.8 to 2	2	1 to 20
Surface area (m <sup>2</sup> /g)	10 to 20	5 to 12	3 to 5	2.6 to 35
Typical particle shape(s)	Platy, bookettes	Irregular - “blocky”	Coccolith, rounded	Platy
Aspect ratio (length/width)	4 to 30	1 to 1.5	1 to 1.5	5 to 20
Reflectivity (%; 547 nm light)	80 to 90	95	88	78 to 93
Abrasion (Einleiner)	2 to 5	4 to 8	-	3 to 5

### Broad Particle Size Distributions

In comparison to the synthetic filler products to be discussed later, natural, ground filler materials tend to have relatively broad particle size distributions (Hagemeyer 1984). Indeed, broad distributions of particle size appear to be a normal consequence of grinding. Whether or not having a broad distribution of particle size makes a difference depends on the application. In the coating of paper, a broad particle size distribution can be an advantage, leading to lower viscosity of suspensions at a given solids content (Xu and Keller 2003; Willoughby *et al.* 2004). Also, a mixture of different-sized particles can pack together more efficiently, forming a denser layer.

For purposes of paper filling, it can be argued, based on theory, that it might be best if all of the particles were approximately equal in size. Exceptionally large particles in a mixture of filler particles tend to contribute to higher abrasivity (Chang and Henderson 1987; Laufmann and Rapp 1995). On the other hand, very small particles, due to their high surface area per unit mass, can increase the demand for various chemical additives, such as sizing agents and retention aids (Krogerus 1999). In addition, as will be discussed later, the optical performance of fillers tends to be best at an optimum size, which also depends on the shape and other conditions of processing.

## Ground Limestone

Commonly known as “GCC,” ground calcium carbonate filler products are obtained mainly from limestone deposits (Hagemeyer 1984; Strutz *et al.* 1988; Huggenberger and Neubold 1997). High quality limestone, having high brightness and suitably low levels of impurities, are widely available. Most limestones were formed by deposition of shells and skeletons of microscopic organisms in shallow seas about 220 to 500 million years ago (Gill and Hagemeyer 1983).

Because limestone is a moderately hard material, having a Moh’s number of 3 to 4 (Wypych 1999), the mining process requires hammering or blasting to release material from the rock formation. The process is continued with grinding, resulting in a range of product classes having different mean particle sizes. Grinding aid chemicals, which include phosphate and polyacrylate dispersants, are added during the grinding process. These additives not only help in the processing of the mineral, but they also serve as dispersants for the resulting fine particles. The origin of the negative surface charge of many GCC products, which affects their subsequent behavior as wet-end additives, can be traced to this use of dispersants.

For use in paper filling applications, two of the most popular size classes of GCC are fine ground (70% < 2  $\mu\text{m}$ ) and ultrafine ground (90% < 2  $\mu\text{m}$ ) (Gill and Hagemeyer 1983). In some cases, fractionation is carried out in order to exclude relatively large particles, which tend to be abrasive. As described later, expected benefits of such processing include more efficient scattering of light.

Some of the primary selling points of GCC are its relatively high brightness and low cost. In addition to these advantages, GCC is said to give faster drainage and reduced energy of drying (Laufmann *et al.* 2000), especially in comparison to unfilled paper. Relatively coarse GCC products tend to yield relatively strong paper at a given filler content, as well as low demand for sizing agents, compared to various other kinds of filler. Such advantages might possibly be attributed to a relatively low surface area of typical commercial GCC products, especially if efforts have been made to narrow the particle size distribution.

## Chalk

Another major class of calcium carbonate filler comes from chalk, a natural deposit formed from the shells of microscopic marine organisms (coccoliths) laid down 30 to 70 million years ago (Dunlop-Jones and Jaycock 1981). High quality chalk deposits are found in England, Denmark, France, and Belgium (Dunlop-Jones and Jaycock 1981). Chalk started to become widely used in Europe as a paper filler during the 1960s (Burke 1993), propelling an early emergence of alkaline papermaking in that region. Though less bright than the later-developed limestone products described above, market expectation for brightness were less demanding than today. Chalk also is noted for having less adverse effect on strength compared to many of the other filler types to be described.

Because of their origin as shells, chalk deposits require much less grinding energy, compared to the limestone products just described. Moreover, the size of individual particles of chalk are more or less pre-determined by the shell-forming processes occurring in ancient sea beds. The distribution of particle size, though broader than some of the

synthetic filler particles to be described later, tends to be have much less of a tail in the direction of very fine particles. For this reason, the surface area of typical chalk filler products tends to be in the range of about 3 to 5 m<sup>2</sup>/g (Fairchild and Clark 1996), which is lower than typical grades of ground limestone, clay, and the most widely used precipitated filler products to be described later. Crude chalk may contain relatively intact prehistoric shells, known as coccoliths, but these are at least partly broken apart during the grinding, which is a necessary step in preparing this material for the filling of paper.

### **Kaolin Clay**

Named for a hill in China, from which porcelain-quality clay was mined in ancient times, kaolin also has a long history as a filler for papermaking. The term “China clay” has long been used to refer to this product, while the technical term kaolinite is useful for referring to the pure mineral. Kaolinite is a platy aluminum silicate material, which is found in sedimentary and metamorphic deposits (Sennett 1997). During the early 1900s clay became the dominant paper filler, and it remains a major resource for papermaking, especially in aqueous coating of paper, in addition to its continuing role as a papermaking wet-end additive (Harben and Virta 1999).

In the US, the best clay deposits are located in Georgia and South Carolina. The sedimentary deposits were laid down by ancient glacial streams. The clay platelets became naturally fractionated as the streams entered shallow prehistoric seas and the currents gradually slowed. In other areas, such as the Cornwall region of Wales in the United Kingdom, the kaolin used as a papermaking material was formed in-situ by natural leaching of related minerals. More recently, high-purity sedimentary clay from Brazil has become available (Powers 1998; Pleeth 2000).

Clay deposits in the US typically are mined by excavation, following the beds of sediment. The clay is typically extracted with a drag line or with back hoes and then hauled to a plunger, which is essentially a high-shear mixer. The resulting slurry is then pumped to a processing facility. The crude clay tends to exist as “books” of clay platelets stacked together. These books are separated, to a varying extent, as the clay is ground and beneficiated into forms suitable for different applications. The typical ratio of width to thickness (aspect ratio) of filler clays is within the range of 4 to 12 (Slepetys and Cleland 1993; Sennett 1997; Beckett *et al.* 1997). The most important processes for beneficiation of clay include screening, fractionation according to sedimentation properties, bleaching, and magnetic removal of certain dark impurities. Such processing is required to achieve reproducible fractions and engineered kaolin products suitable for different applications (Murray and Kogel 2005). Jameson and Sennett (1989) described how a flotation process can also be used to remove some of these colored impurities. Some clay is subjected to a milling process with fine ceramic media; this process, known as delamination, results in further division of the clay into yet thinner platelets, having aspect ratios in the range of 10 to 30.

As a filler for paper, some of the most favorable attributes of kaolin include its ease of dispersal in water (especially in the presence of phosphate, as a dispersing agent), its relatively low abrasivity (if pure), and its brightness, which was considered quite adequate until the emergence of calcium carbonate fillers in the last three decades. Though the edges of purified clay platelets appear to have a positive charge (Solomon and Hawthorne 1983),

the presence of dispersing agents renders the zeta potential strongly negative in most commercially available kaolin products.

The properties of clay can vary considerably, depending on their source and the degree to which they have been processed (Velho and Gomes 1995). The presence of iron in certain clay products has been reported to be responsible for the darkening of mechanical pulp fibers (Narvestad *et al.* 2013). The authors recommended avoiding a long contact time between such clay and mechanical pulp slurry before formation of the paper.

### **Calcined Clay**

A brighter, bulkier material can be produced by subjecting ordinary (hydrous) kaolin to the intense heat of a furnace (Drzal *et al.* 1983; Dubois *et al.* 1995). A similar treatment can be applied to such materials as talc or aluminum trihydrate, with similar effects on brightness and bulk (Mahapatra and Patel 1994). The term calcination comes from the fact that the equipment used for this heating process is the same as what is used to convert calcium carbonate mineral to calcium oxide – a process that will be mentioned again in a later discussion of precipitated calcium carbonate filler. The calcination process, usually involving a temperature above 950 °C (Drzal *et al.* 1983), not only results in a loss of water of hydration from the clay mineral structure, but it also causes the clay particles to become fused together. After cooling, the resulting powder is usually ground and fractionated again. The bulky nature of calcined clay can be attributed to the composite structure, which resists tight packing. The relatively high light-scattering ability of calcined clay has been attributed to the random orientations of fine-particle-size clay plates fused together in a way that creates a large area of air-solid interfaces (Bauch 1992).

### **Chemically-Structured Kaolin**

In an effort to avoid both the high cost and the abrasive quality resulting from calcinations of kaolin clay, various authors have reported strategies based on chemical agglomeration of clays and other minerals (Bundy *et al.* 1986; Pratt *et al.* 1988; Johns *et al.* 1990). The usual goal of this treatment is either to achieve bulking characteristics similar to calcined mineral products, or to minimize the adverse effects of filler addition on paper strength properties.

To achieve results intermediate between ordinary (hydrous) clay and calcined clay, the particles may be agglomerated by polyelectrolytes such as poly-diallyldimethylammonium chloride (Pratt *et al.* 1988; Slepetyts and Morgan 1991). These studies have shown that the most effective agglomeration requires a polymer dosage of about 0.1 to 0.3% by mass, based on solids, which is consistent with a charge neutralization or charged patch mechanism. The resulting aggregates were found to have random orientations of plates, improving the bulking characteristics of the mineral (Slepetyts and Morgan 1991). A related method involves treatment with an amine, such as hexamethylenediamine, followed by in-situ precipitation of aluminum hydroxide onto the kaolin, with specific adjustments of pH (Bundy *et al.* 1990). The agglomerated minerals may be subjected to subsequent processing steps such as acidification, bleaching, washing, and treatment with a phosphate-type dispersing agent (Nemeh and Slepetyts 1988). Similar approaches have been used in the formation of composite mineral products, for instance with a combination of clay and titanium dioxide (Carter and Holton 1993). The cationic treatment causes the

titanium dioxide particles to be spaced over the surfaces of the clay platelets, yielding good optical efficiency, in addition to good retention during the formation of paper.

### **Talc**

Talc is best known to papermakers as a detackifier, and it is widely used in efforts to combat the effects of pitch and sticky materials in papermaking processes (Valero and Holton 1995; Trivedi 1997). However, talc is also widely used as a filler, especially in Finland, Japan, China, and France, where high-quality deposits are located (Biza 1999). Talc is notable for its softness (no. 1 on the Moh scale), for its oil-loving character, and for its platy particle shape. Chauhan and Bhardwaj (2013) found that adding talc, as a filler, to handsheets contributed to their hydrophobicity. Talc's surface free-energy is in the range 35 to 68 mNm<sup>-1</sup>, which means that one can expect a finite contact angle of water on a talc surface. A wetting agent, such as a nonionic surfactant, is required for good dispersal in water (Trivedi 1997).

In the US, industrial talc mainly comes from Montana. Fine-particle talc is preferred for detackification of pitch and sticky materials. In such applications an addition rate of at least 5 to 7.5 kg (less than 1.0% by mass) of talc per tonne of paper is recommended (Rooks 1993), since insufficient amounts may merely add to the mass of tacky deposits without solving the problems.

When it is used at high enough levels to earn the label “filler,” rather than just a “control agent for pitch and stickies,” talc can benefit various paper properties (Biza 1999). For instance, the uniformity of color can benefit from talc usage, especially in cases where strong mineral-to-dye affinity is needed in order to achieve an even-sided sheet. The relatively large, water-resistant particles of filler-grade talc are said to promote more rapid dewatering of paper. The alignment of talc particles at the paper surface can help to reduce paper's coefficient of friction and also improve barrier properties of certain paper products (Biza 1999).

### **Mica**

Sericite mica has been used as a filler for paper in areas such as Taiwan, where it is prevalent. A recent study showed that sericite can resemble montmorillonite (bentonite) in its ability to swell and delaminate in water, especially if the positive ions are replaced by sodium (Perng and Wang 2004). In spite of the fact that the planar dimensions of the sericite particles are larger than typical filler particles, such as clay, it was found that they can act like “microparticles” (*e.g.* bentonite, colloidal silica, *etc.*) in terms of their effect on wet end operations. In other words, sequential addition of sericite filler and cationic acrylamide copolymer retention aid resulted in enhanced drainage and retention (Perng and Wang 2004).

### **Zeolites**

Zeolite products, due to their naturally porous nature, have potential to act as absorbents for various contaminants, or inks, *etc.* (Ivanov and Heinzl 1996; Ivanov *et al.* 1996; Sain *et al.* 2001; Gregor-Svetec *et al.* 2012). For example, zeolite-filled paper has been shown to be effective for adsorption of radioactive cesium during decontamination operations (Toppan 2015). The performance of zeolite as a collector of organic

contaminants was found to improve when it was treated with polyaluminum chloride (PAC), giving the particles a positive zeta potential (Sain *et al.* 2001). Gregor-Svetec *et al.* (2012) reported gains in printability with the addition of zeolite as a filler.

### Diatomaceous Earth

Another mined product used occasionally as a filler is diatomaceous earth. Deposits of this mineral, composed primarily of silica, were formed from the skeletons of aquatic plants. A high internal porosity and abrasive nature makes these materials promising for deposit control. Their brightness and other properties related to paper filling can be improved by calcining and other beneficiation processes (Cho *et al.* 1995).

## SYNTHETIC, PRECIPITATED FILLER PRODUCTS

Table 5 summarizes typical values for four types of synthetic minerals often used as fillers for paper (Gill and Hagemeyer 1983; Wypych 1999). In each of the cases shown, the original mined source material becomes dissolved and later precipitated into a different form.

**Table 5.** Typical Properties of Four Major Synthetic Papermaking Fillers

Product Type	PCC (calcite)	TiO <sub>2</sub> (rutile)	Al(OH) <sub>3</sub> ("ATH")	CaSO <sub>4</sub> · 2H <sub>2</sub> O
Density (g/cm <sup>3</sup> )	2.7 to 2.9	4.24	2.4	2.3 to 3
Hardness (Moh's scale)	3 to 4	6 to 7	2.5 to 3.5	2 to 3
Loss on ignition (%)	43.5	0 to 2	34.6	various
Refractive index	1.48, 1.65, 1.7	2.7	1.58	1.52 to 1.61
Mean diameter (µm)	0.8 to 2	0.3 to 0.35	0.5 to 1	6
Surface area (m <sup>2</sup> /g)	4 to 25	-	8 to 16	-
Typical particle shape(s)	rosette; blocky	rounded	rounded	needle
Aspect ratio (length/width)	1 to 1.5	1 to 1.5	1 to 1.5	10
Reflectivity (547 nm light)	98 to 99	98	99 to 100	90 to 92
Abrasion (Einleiner)	3 to 5	30	1 to 3	6 to 8

Precipitated calcium carbonate (PCC), and titanium dioxide (TiO<sub>2</sub>) are the best known synthetic mineral products used as paper fillers. However, the short list in Table 5 hardly exhausts the possibilities available for paper products with special property requirements. A common feature of synthetic types of fillers is that they result from chemical precipitation reactions, in which positive and negative ionic species come out of solution to form a relatively insoluble compound. By adjusting the ion concentrations, the temperature, and various minor additives, the manufacturer has many ways to influence the particle characteristics.

Though there are many exceptions, it is possible to make some general statements comparing synthetic mineral fillers to their natural counterparts, especially in cases where both forms of a given mineral are available for use as fillers. Because of the way in which they are produced, the particle size distributions of synthetic minerals tend to be narrower

(Gill 1989; Fairchild 1992). Likewise, the process of forming a solution, from which the final product is precipitated, can make it possible to remove impurities, including abrasive particles. As noted by Stark and Eichinger (1985) the freshly-prepared surfaces of synthetic minerals generally can be expected to have a higher free energy per unit of surface area, causing those surfaces to have higher affinity for various materials in solution.

### Precipitated Calcium Carbonate (PCC)

Starting in the early 1980's, precipitated calcium carbonate has grown from relative obscurity to become by far the most widely used filler for paper (Tøttrup 1999). This is especially true in the US, where PCC usage increased to about 70% of all of the filler use by mass (Gill 2004). PCC also increased its market share in Europe (Tøttrup 1999).

A key motivation behind the growth of PCC use as a papermaking filler in the US has been the "cost of opacity" (Williams and Gill 1992). Prior to the 1980s, papermakers' main strategy for increasing the opacity of printing papers, especially at low basis weights, was to increase the content of  $\text{TiO}_2$  (see later), which was used in combination with clay filler. But the cost of  $\text{TiO}_2$  can be roughly 5 to 10 times higher than that of other commonly used fillers. The higher light scattering ability of PCC, compared to clay, made it possible for papermakers to achieve their opacity and brightness targets without  $\text{TiO}_2$ .

The main source material for manufacture of PCC is limestone, as in the case of the GCC products discussed earlier. However, in the case of PCC the original limestone powder undergoes calcination, a process that drives off 44% of the mineral's original mass. The resulting lime,  $\text{CaO}$ , is then transported to the point of PCC synthesis. The term "satellite plant" refers to the common practice of locating the PCC manufacturing operation adjacent to a paper mill where the filler is to be used (Gill 1988). In this way, the mass of transported material is kept to a minimum. A further economic advantage of the satellite concept can be gained by using smokestack exhaust as a source of the  $\text{CO}_2$  gas used in subsequent steps in the synthesis process.

The precipitation process for PCC starts with slaking, which is the addition of water to finely ground  $\text{CaO}$  (Laine 1980). Reaction of the lime with water yields  $\text{Ca(OH)}_2$  particles, sometimes known as milk of lime. This mixture is exposed to the  $\text{CO}_2$  gas, which gradually lowers the pH as it converts the  $\text{Ca(OH)}_2$  into  $\text{CaCO}_3$ . Factors that affect the size and shape of the resulting particles include the overall concentration, temperatures, agitation, pH, and addition of other soluble materials (Hagemeyer 1984). Lower water temperatures tend to result in blocky (rhombohedral), discrete particles of the calcite mineral form, whereas higher temperatures tend to yield a rosette-shaped composite form of calcite, known as scalenohedral PCC.

Due to the presence of relatively high levels of silica in certain non-wood fiber species, lime mud produced during kraft pulping may not be suitable for the usual chemical recovery cycle; as a consequence there is a strong motivation to find other uses for it. Peng *et al.* (2015) described experiments in which lime mud having a relatively high silica content was precipitated by a cationic acrylamide copolymer flocculant and then added to a fiber furnish. Such preflocculated lime mud yielded paper with greater efficiency of hydrophobic sizing in comparison to untreated lime mud (Peng *et al.* 2014). Also, the paper strength was higher than with untreated lime mud (Peng *et al.* 2015).

Koivunen *et al.* (2009) and Koivunen and Paulapuro (2010) experimented with a way to improve the light scattering ability of PCC filler. By inclusion of Zn and Sr during mineral preparation, a higher refractive index was achieved. Lourenço *et al.* (2013; 2014) treated PCC surfaces by subsequent precipitation of silica, and they attributed the resulting strength improvements of paper to improved hydrogen bonding.

### Aragonite

Although aragonite is a form of PCC, having the same chemical formula as the calcium carbonate products discussed up to this point, it has a different arrangement of the atoms in the crystal (Laine 1980; Dunlop-Jones and Jaycock 1981; Anderson and Yunko 1983; Hagemeyer 1984; Konno *et al.* 2007; Hu *et al.* 2009). It is generally formed in the same manner as calcite, but with higher temperatures of processing. The acicular particles of aragonite PCC are sometimes described as “needles,” although that word has to be considered as an exaggeration, since a typical length-to-thickness ratio of the elongated particles is about 5. Often the primary particles are fused together in rosettes. Though the main papermaking applications of aragonite PCC have been in mineral coatings, it is clear that aragonite products also can be used as fillers. Hu *et al.* (2009) reported favorable strength results and satisfactory optical properties. Wang *et al.* (2012) showed that rod-shaped calcium carbonate particles could be prepared during processing of lime mud. Hu *et al.* (2009) showed that favorable strength results could be achieved by taking advantage of the somewhat fibrillary nature of aragonite. Chen *et al.* (2011b) reported relatively high retention when using relatively long (20 to 60  $\mu\text{m}$ ) aragonite crystals instead of ordinary PCC in filled paper sheet; furthermore, the sheets with the large aragonite particles showed higher strength in comparison to sheets with the default PCC, especially when the filler content was above 10%. Konno *et al.* (2007) and Nanri *et al.* (2008) showed the feasibility of forming high-quality aragonite particles by employing the causticizing facilities of a conventional kraft pulp mill.

### Acid-Tolerant PCC

Paper grades that contain substantial amounts of high-yield pulp, such as thermomechanical pulp (TMP), have tended to resist the transition to the use of calcium carbonate filler. A contributing reason for this resistance is a phenomenon known as alkaline darkening (Poirier *et al.* 1996). Exposure of high-yield mechanical pulp to alkaline pH conditions yields substantial loss of brightness, with the degree of darkening dependent on such factors as the fiber species and the ionic content of the water. Because ordinary calcium carbonate fillers dissolve when the pH is below about 6.5, acidic conditions must be avoided. To overcome this limitation,  $\text{CaCO}_3$  particles have been treated with phosphates and other chemicals to make them resist dissolution. The resulting “acid-tolerant PCC” has been found to yield satisfactory brightness (Mathur and Lasmarias 1991; Evans *et al.* 1991; Ain and Laleg 1997; Shen *et al.* 2009a,b,c). Another goal of acid-tolerant technology has been to allow the use of rosin and alum in the presence of calcium carbonate (Mather and Lasmarias 1991; Patel and Panigrahy 1996a,b).

Various related strategies have been employed to prepare acid-tolerant calcium carbonate slurries. Pang *et al.* (2003) investigated the mechanism by which phosphate treatment retards to dissolution of  $\text{CaCO}_3$ . They concluded that a layer of calcium

phosphate precipitates from solution onto the particles, forming a protective barrier. It was recommended to allow sufficient treatment time after treatment in order to build up an adequate barrier before the mineral is exposed to acidic conditions of papermaking. Other dissolution-inhibiting additives include magnesium ions, 1,2-dicarboxylic acids, oxalate, and orthophosphate (Pang *et al.* 1998). Tokarz *et al.* (1990) described a process in which sodium silicate solution was added to PCC slurry, followed by adjustment of the pH to about 9.3, and then followed by acidification with  $\text{ZnCl}_2$ . This procedure yielded a silicate coating of the particles, rendering them tolerant of lower pH values.

### Titanium Dioxide

Highly prized for its ability to scatter light,  $\text{TiO}_2$  has found its greatest use as a filler in relatively light-weight grades of paper that nevertheless have demanding requirements for opacity (Kwoka 1997). Paper for religious texts is a prime example. Another key use is in waxed or highly densified products, since other commonly used fillers lose most of their ability to scatter light in the absence of air spaces surrounding them.  $\text{TiO}_2$ 's unique ability to scatter light even in the absence of air spaces is a consequence of its much higher index of refraction, compared to most other solid materials commonly used in papermaking. Refractive index can be described roughly as a material's ability to cause light to bend, as in the case of a prism or lens. A related attribute of  $\text{TiO}_2$  is its tendency to absorb ultraviolet (UV) light. Though the absorption of UV light can reduce the photo-yellowing of high-yield fibers (Kwoka 1997), the down-side is that fluorescent whitening agents (FWAs), which depend on UV light, become less effective in the presence of  $\text{TiO}_2$ .

Depending on the procedures used for its synthesis (Solomon and Hawthorne 1983),  $\text{TiO}_2$  can be formed as either of two distinct crystalline forms, rutile and anatase. Of these two, rutile has the higher refractive index (2.7, vs. 2.55), higher hardness (6 to 7 vs. 5 to 6), and greater tendency to adsorb UV light (Wypych 1999). These differences, though subtle, tend to cause some differentiation according to paper grade. Rutile is especially used in grades that require the highest opacifying efficiency, with less emphasis on the paper's brightness. Anatase, because it does not absorb as much in the near-UV and far-blue parts of the spectrum, contributes less yellowness to the paper, compared to rutile. Also, it competes less strongly for UV light with fluorescent whitening agents, compared to rutile  $\text{TiO}_2$ .

### Aluminum Trihydroxide

This product, often called "ATH," is a pure white pigment, sometimes used in production of paper grades requiring the highest practical level of brightness (Koenig and Tauth 1984; Healy and Kramer 1997; Chen *et al.* 2011a). The particles are typically very small and spherical, though somewhat larger than widely available  $\text{TiO}_2$  particles. Sometimes ATH is used as an "extender" for  $\text{TiO}_2$ , helping to space the higher-refractive index particles apart from each other to achieve better optical efficiency (Healy and Kramer 1997). Chen *et al.* (2011a) showed that addition of ATH to paper can achieve greater tolerance to high-temperature treatment (*e.g.* flame retardancy). Sha and Chen (2014) considered an alternative approach to achieving flame retardant effects using a phosphate treatment of diatomite silica particles for use as paper fillers.

The common way to prepare ATH begins with solubilization of bauxite ore in NaOH (Healy and Kramer 1997). Iron oxide is separated as a sediment. Seed crystals of ATH are then added to the solution as it cools, promoting further precipitation of ATH. Indiscriminate use of aluminum sulfate in paper machine systems, especially when it inadvertently comes into contact with water of neutral or alkaline pH, can result in deposition of scale material having approximately the same chemical formula as ATH, *i.e.* Al(OH)<sub>3</sub>.

### **Amorphous Silica Fillers**

Amorphous silica is produced by the controlled acidification of sodium silicate solution (Crawford and Alderfer 1990; Alderfer and Crawford 1997). Each observable particle consists of a huge number of silica nano-spheres fused together in a solid gel structure, giving a high specific surface area and internal void spaces. An important application is for absorption of ink-jet fluids, especially in high-end applications.

### **Amorphous Silicate Fillers**

Synthetic amorphous silicate products, though similar in chemistry to ordinary kaolin clay, tend to have much higher surface area per unit mass, in addition to being highly porous. As noted by Koga and Taga (1993), such products with pores in the size range 0.3 to 4 μm can be very effective for absorbing the vehicle of printing inks.

Silicate chemistry also has been used as a means of coating natural filler materials to improve their properties (Novak 1982). To accomplish this, calcium chloride solution was combined with sodium silicate in the presence of the mineral slurry. The reported surface areas, in the range of 85 to 145 m<sup>2</sup>/g, were much higher, relative to the starting material. Brightness was increased and abrasivity was reduced.

A new class of internally fibrous mineral particles based on calcium silicate has been reported (Mather and Joyce 2004). Conditions of precipitation of these products allow considerable control over particle morphology.

### **Calcium Silicate**

Another product related to the earlier discussion of high-temperature incineration is fly ash, a material that is largely composed of silica and calcium silicate (*e.g.* Ca<sub>2</sub>O<sub>4</sub>Si). Filler-grade calcium silicate from this source can be regarded as a synthetic, precipitated mineral product due to the fact that the fly ash is subjected to strong alkali, which dissolves the silica content. Addition of CaO particles then yields calcium silicate. Song *et al.* (2012) and Zhang *et al.* (2013) evaluated its use as a filler for paper. The brightness is lower than that of a typical grade of commercial precipitated calcium carbonate; however the fly ash yielded higher strength and lower apparent density in the resulting paper.

### **Synthetic Gypsum**

Calcium sulfate dihydrate, otherwise known as gypsum, has many positive attributes as a filler, and its cost can be among the lowest of the available filler materials. Gypsum is bright, soft, and capable of being prepared in different particle shapes in a favorable range of sizes for use as fillers. The most typical form of crystals are needle-shaped (acicular), having a length-to-diameter ratio of about 4 to 10 (Gussinyer 1986).

Gypsum can be prepared with a positive zeta potential, which is expected to be beneficial for its retention during the formation of paper.

The one main perceived deficiency of gypsum has been its solubility in water. Approximately 2 to 4 grams per liter of the dehydrate will dissolve under papermaking conditions (Hofmann *et al.* 1990). On the one hand, such dissolution may be considered as a waste of material. On the other hand, the high degree of recirculation in modern white water systems is expected to lead to a saturated condition of the ions in solution, limiting further dissolution (Gussinyer 1980). Gussinyer and Gussinyer (1999) proposed a mechanism whereby evaporation of saturated solution during the drying of paper tends to fuse the ends of gypsum crystals onto adjacent cellulosic fibers, creating a permanent bond.

### **Urea-Formaldehyde Pigment – A Non-Mineral Filler**

A non-mineral filler having superior optical properties can be prepared as a condensation product of urea and formaldehyde (Menashi *et al.* 1978; Kramer 1993). After the reaction, the material is aged, milled, neutralized with NaOH, washed, and then milled to the final size (Kramer and Haller 1993). Due to their internal void structure, the UF pigments can achieve a remarkable combination of light scattering ability, bulking ability, and an ability to absorb organic vehicles of some printing inks. The light scattering ability can be almost as high as that of TiO<sub>2</sub>, despite a much lower refractive index. Another advantage is that UF pigments do not absorb ultraviolet light, making them suitable for use in combination with fluorescent whitening agents (FWAs). The adverse impact on strength was found to be less, compared to other commonly used fillers (Kramer 1993).

### **Starch as a Filler?**

Under normal conditions of preparation, starch products are either added to the papermaking process in soluble form or, if added in granular form, the starch tends to cook when the paper is dried, contributing to the strength of paper. However Krogerus (1999) showed that starch could be used as a filler. The starch was rendered non-swelling by cross-linking and cationized, or by grafting with styrene groups. The starch granules were reported to contribute to paper's opacity, as in the case of mineral fillers. Koivunen *et al.* (2010) showed that the optical performance of starch granules, when used as a paper filler, can be improved by "spot welding" their surfaces with aluminum silicate particles. Research related to the use of renewable organic materials as fillers for paper has been reviewed by Shen *et al.* (2011). Kim *et al.* (2015) considered the use of various lignocellulosic powders as fillers and showed that the strength of the resulting paper could be improved by treatment of the particle surfaces with cationic starch. The general topic of organic fillers for papermaking has been reviewed by Shen *et al.* (2010a).

### **Recovery of Filler from Paper Mill Waste Sludge**

There is a potential source of "free," but contaminated filler material in the sludge from primary wastewater clarifiers for paper mills, especially in cases where there are de-inking operations. Sohara and Westwood (1997) showed that ash from a boiler fed with waste sludge could be used as a source of calcium for the production of PCC; however the resulting product was not as bright as regular PCC. Likewise, Moilanen *et al.* (2000) showed that waste sludge from papermaking could be incinerated in a rotating kiln,

followed by treatment with CO<sub>2</sub> (carbonation) to recover calcium carbonate filler of acceptable brightness. Johnston *et al.* (2000) described a two-step treatment in which such sludge was oxidized under alkaline conditions to get rid of the stickies, after which it was subjected to further hydrothermal treatment to get rid of colorants, allowing the mineral to be reused in paper.

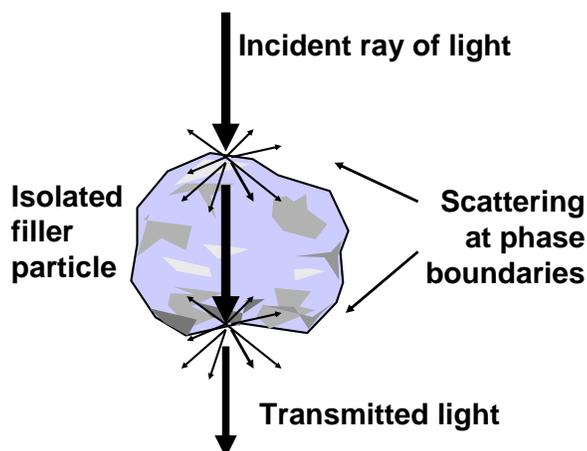
## HOW FILLER AFFECTS PAPER PROPERTIES

Having just introduced some of the most important filler products for papermaking, it is worth considering ways in which fillers affect paper properties. Various theories, to be summarized here, have been developed for application across a broad range of filler types.

### Optical and Strength Properties

The reason for considering filler's effects on optical and strength properties together, rather than one at a time, is due to a striking inverse relationship which has been observed between these two kinds of effects (Davidson 1965; Beazley and Petereit 1975). According to Page's theory (1969), paper's tensile strength depends on both the strengths of the fibers and also the strength of the bonds between the fibers. In the case of a typical sheet of paper for printing or packaging, the inter-fiber bonds are expected to be the main point of failure when strips of paper are pulled past their point of breakage. Page proposed that the strength of inter-fiber bonds depended on a variety of factors. Two of the most critical factors, related to bonding, are the relative bonded area between fibers and the adhesive strength per unit of bonded area. In principle, fillers can be expected to affect each of these two factors.

Figure 4 shows a much-simplified, but still useful representation of what happens when a narrow beam of light strikes an isolated filler particle.



**Fig. 4.** Schematic representation of light scattering events as a narrow beam of light passes through an isolated filler particle

Assuming that the particle is large relative to the wavelength of the light (which is seldom completely true in the case of fillers), one can picture two light-scattering “events.” The first occurs when the beam experiences the change in refractive index upon passing from the surrounding medium into the front of the filler particle, and the second event occurs as the beam exits the other side. The word “scattered” is used instead of “refracted,” since one is generally dealing with collections of odd-shaped, rough, prism-like objects that are not large relative to the wavelength of the incident light.

According to theory, one expects essentially no scattering of light from regions in a paper sheet where adjacent cellulosic surfaces are in optical contact. The words “optical contact” mean, in effect, that surfaces are less than about 0.2  $\mu\text{m}$  of each other, a fraction of a wavelength of visible light. It has been argued that surface tension forces, during the drying of paper, are sufficiently strong so that adjacent cellulosic surfaces at such distances will essentially “snap together” into true molecular contact (Ratliff 1949; Campbell 1959).

Figure 5 illustrates how the presence of a filler particle between two adjacent fibers might be expected to affect a beam of light as it passes through a sheet of paper. It is worth noting that relatively little scattering of light is expected if the beam passes between materials of similar refractive index, *e.g.* fiber-filler-fiber. By contrast, more scattering of light is expected if the filler particle debonds the paper structure, so that a representative beam of light encounters more changes in refractive index, *e.g.* fiber-to-air or filler-to-air.

### **Filler Content vs. Paper Strength**

Bøhmer, in his review article (1981), states that addition of 10 percent filler by mass is expected to result in 20 to 25% loss in tensile or burst strength of paper. Experience has shown, however, that there can be wide variations from this rule of thumb. Some paper properties, such as folding endurance, appear especially vulnerable to the effects of filler addition. Also, the degree of strength loss depends on many variables, including the properties of the filler.

### **Particle Size vs. Strength**

In general it has been found that the debonding effect of fillers increases with decreasing particle size (Bown 1981; Lindström *et al.* 1985; Gill 1990a,b; Bown 1998). One explanation for this effect is that smaller filler particles have a higher surface area per unit of mass. Not only are the smaller fillers able to cover up more of the fiber surfaces, interfering with direct contact between adjacent fibers, but also there is a larger net amount of surface area available to be covered by any bond-enhancing polymers, such as hemicellulose and cationic starch. Lindström *et al.* (1985) showed that it was possible to overcome the adverse effect of fine fillers on paper strength by adding massive amounts of cationic starch. The high addition level, as well as the high density of the resulting paper, suggests that the mixture of starch and filler was acting as a binder in a composite structure, such that starch fills the void areas created by the filler particles.

### **An Optimum Particle Size for Optical Properties**

Huber (1970) reviewed early studies suggesting that there is an optimum in particle size for the most efficient light scattering. Bown (1981) found that light scattering increased with decreasing particle size of filler, down to about 0.7  $\mu\text{m}$ . It was concluded

that the increase in light scattering was due to (a) an inherently greater light scattering ability of the smaller particles, due to their greater air-solid interfacial area, (b) the fact that smaller particles are able to hold more cellulosic material apart from each other, preserving air spaces adjacent to the particles, and (c) the fact that the filler particles also can prevent fibrils from coming together due to capillary forces that act during the drying of paper. In the case of platy clay particles, Koppelman (1981) reported the most efficient light scattering when the equivalent spherical diameters were within the range of 0.7 to 1.5  $\mu\text{m}$ .

Van den Akker (1977) pointed out that at least part of the particle-size dependency of light scattering by papermaking fillers can be explained by physics, using the Mei theory of light scattering. Based on that theory, an isolated, spherical particle is expected to scatter light most efficiently, per unit mass, when the diameter is approximately one-half the wavelength of light, which corresponds to approximately 0.23  $\mu\text{m}$  in the case of blue light. Such a dependency has been confirmed by measurements of light scattering from mineral slurries (Clewell 1941).

Important clues as to the mechanism by which ordinary fillers contribute to paper's light scattering ability were shown in a highly inventive series of experiments reported by Bown (1985a). Sheets were formed from well-refined and slightly-refined fiber batches with a variety of different filler types and levels of filler in the resulting paper. Then, before the paper was tested, non-aqueous solvent was used to dissolve away the fillers without swelling or otherwise disturbing the paper structure. It was found that the void spaces, representing the "missing" filler particles continued to scatter light. This observation implies that much of the effect of fillers on paper's optical properties must be partly due to their influence on paper's microstructure, rather than just their mere presence.

In other studies the optimum particle size for light scattering efficiency has been found to be a function of particle shape (Gill and Scott 1987). For instance, Zeller (1980) found that a particle diameter of 0.4 to 0.5  $\mu\text{m}$  gave the highest light scattering, per unit mass of filler, in the case of blocky rhombohedral PCC particles. By contrast, rosette-shaped scalenohedral calcite gave the best light scattering in the range 0.9 to 1.5  $\mu\text{m}$  of particle diameter. It might be argued, based on such results, that it is not fair to count the side-to-side distance of rosette-shaped particles as the "size," when considering optical effects. If one instead considers the primary particles making up the scalenohedral composite particle, then it is likely that a predicted optimum particle size for light scattering would agree more closely with the results for the rhombohedral PCC. Rosette-shaped particles have a distinct advantage for increasing opacity at relatively high filler levels (Gill and Scott 1987), a result that is consistent with their resistance to packing tightly together.

### Size Optimization of $\text{TiO}_2$ Particles

In the case of  $\text{TiO}_2$  particles the optimum particle size for light scattering is considerably smaller, compared to most other varieties of fillers. Commercial-grade  $\text{TiO}_2$  for papermaking often has a mean diameter of about 0.3 to 0.35  $\mu\text{m}$ , in contrast to about 0.5 to 3.5  $\mu\text{m}$  for most other commonly used fillers. There are two ways to rationalize this difference in particle size, and both involve the fact that  $\text{TiO}_2$  has a much higher refractive index (either 2.55 or 2.7, depending on the crystalline form), compared to the most commonly used fillers (*e.g.* 1.5 to 1.65). The first reason is that  $\text{TiO}_2$ 's effects depend much less on the preservation of air spaces within the paper; there is a significant change

in refractive index if light passes directly from TiO<sub>2</sub> into cellulose or other material having a lower refractive index. Thus, TiO<sub>2</sub> is widely used for the production of opaque, wax-impregnated products, in which essentially no air spaces remain. Another consequence of this effect is that the TiO<sub>2</sub> particles can contribute to opacity in ordinary paper despite the fact that they are too small to brace adjacent cellulosic surfaces very far apart from each other.

A second reason why the optimum particles size for light scattering is smaller in the case of TiO<sub>2</sub> particles, compared to other fillers, is that the speed of light is substantially slower in media of higher refractive index (James and Griffiths 1992). The slowing of light causes successive waves in the light beam to be closer together, much like what happens when traffic slows on a certain stretch of highway, causing cars to be bunched together. A shorter wavelength of light then implies that the light can be scattered effectively by a somewhat smaller particle.

Yet another reason that papermakers and other users of TiO<sub>2</sub> usually prefer very small particles is a matter of cost. The material is more expensive, per unit mass, compared to most CaCO<sub>3</sub>, kaolin, or cellulosic fiber materials. That makes it all the more important to manufacture a particle size that gives the biggest impact on optical properties, per unit mass.

### Light Scattering vs. Bonding in Filled Paper

A semi-quantitative approach to understanding the effects of fillers on both strength and optical properties is possible, based on application of light-scattering theory and the equations of Kubelka and Munk (Robinson 1975; Anon. 1987). The Kubelka-Munk equations can be used to estimate coefficients for the light scattering and light-absorption ability of different filler particles (Middleton *et al.* 1994). Contrary to the most basic form of the theory, the optical efficiencies of various fillers tend to fall as their level in paper is increased. Middleton *et al.* (1994) concluded that the effect is related to increased “agglomeration” of filler in the sheet as the level is increased. Also, the incremental effect of filler on preservation of void spaces within the paper tends to fall with increased levels of filler (see later).

Important evidence indicating the mechanism by which fillers contribute to the opacity of paper was obtained by combining light scattering measurements with mercury porosimetry (Alinec *et al.* 2002). In the cited work the pore size was systematically varied by optional addition of TMP fines, microcrystalline cellulose, and microfibrillated cellulose. Filler addition and flocculating agents were also used to prepare a set of paper sheets having a wide range of both pore size distribution and light scattering ability. Results showed that pore spaces within the paper had to be larger than a critical size of about 0.2 μm in order for there to be a significant contribution to light scattering. In support of these findings, Seo *et al.* (2010) observed a linear relationship between the quantity of voids larger than 0.2 μm and the light scattering ability of paper sheets made from red algae fibers. The same considerations also help to explain an observed relationship between light scattering and sheet density (El-Hosseiny and Abson 1979). A mechanism involving a spacing effect of fillers, preventing the closure of openings between cellulosic surface, is also consistent with the superior light scattering effects of fillers having a low packing density, such as calcined clay and scalenohedral PCC (Bauch 1992).

Further innovative work was carried out by Kinoshita *et al.* (2000), who varied the density of paper by artificially cutting some of the fibers. The bulkiest unfilled sheets were those with a ratio of 1:3 uncut to cut fibers. Addition of filler generally bulked up the paper, especially in the case of uncut fibers. The bigger particles had somewhat higher bulking ability. Tests involving filler contents as high as 70% showed that strength effects were consistent with expected changes in inter-fiber contact areas. Consistent with studies cited earlier, the smaller filler particles had a larger adverse effect on strength at a constant level of filler, *e.g.* 10% by mass.

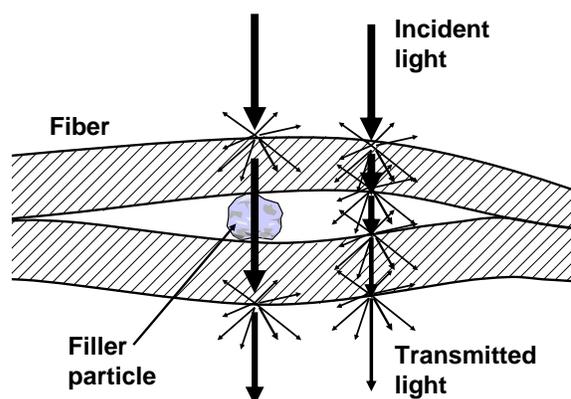
### The Bulking Effect of Fillers vs. Light Scattering and Bonding

Although most of the studies cited in the previous subsection suggest a relatively simple inverse relationship between light scattering and paper strength, when comparing different particle sizes, shapes, and addition levels of various fillers, papermakers have long held out hope for an inexpensive material that would give them the best optical properties at an acceptable level of strength loss. Work by Phipps (2001) and by Doelle and Amaya (2012) suggests that the winners in this kind of horse-race among different filler products tend to be won, though not by a large margin, by particles that do not pack tightly. Examples include rosette-type and rhombohedral-type PCC, especially in cases where these products have a relatively narrow particle-size distribution. Supporting evidence of similar nature has been provided by Gill (1989). The relatively high light scattering of a certain premium-grade, fine-particle-size rhombohedral PCC appears to involve a combination of ideal particle diameter (*ca.* 0.3  $\mu\text{m}$ ) and an inability of the particles to pack tightly (Passaretti *et al.* 1993). Fairchild (1992) found that the best combination of strength and optical properties at relatively high filler levels could be achieved by a so-called “clustered prismatic” structure, which is something of a compromise between a rosette structure and a condensed, rounded structure.

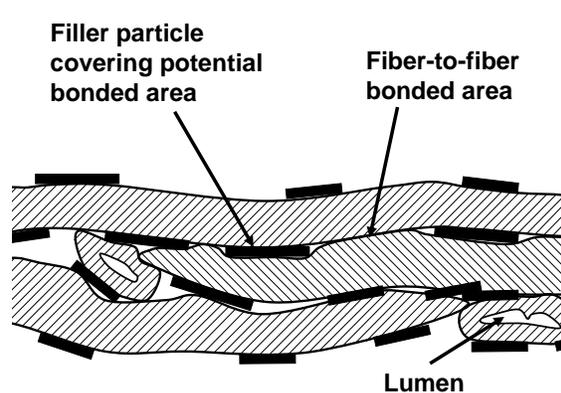
#### *Bracing and covering*

One of the best explanations for why bulky fillers (those having a low packing density) tend to have larger effects on paper strength and optical characteristics was offered by Beazley and Petereit (1975) and others (Bown 1983; Stark and Eichinger 1990; Adams 1993; Krogerus 1999). As illustrated in Figs. 5 and 6, it was proposed that there are basically two main mechanisms by which fillers interfere with the strength of paper. Figure 5 illustrates one of those mechanisms, which we will call the “bracing” mechanism. Bracing means that a filler particle interposed between adjacent fibers will tend to increase the average distance between them.

The second mechanism, which can be called the “covering” mechanism, is illustrated in Fig. 6. The covering mechanism involves the fact that fillers interposed between adjacent cellulosic surfaces prevent direct contact between those surfaces. Though various types of bonding, including hydrogen bonding, can take place between a cellulosic surface and a filler particle, such bonds are not expected to match the strength that can be achieved by direct fiber-to-fiber contact. This is because polymer chains associated with adjacent cellulosic surfaces are able to interpenetrate before the paper is dried, thus forming a three-dimensional zone of adhesion (McKenzie 1984; Pelton 1993).

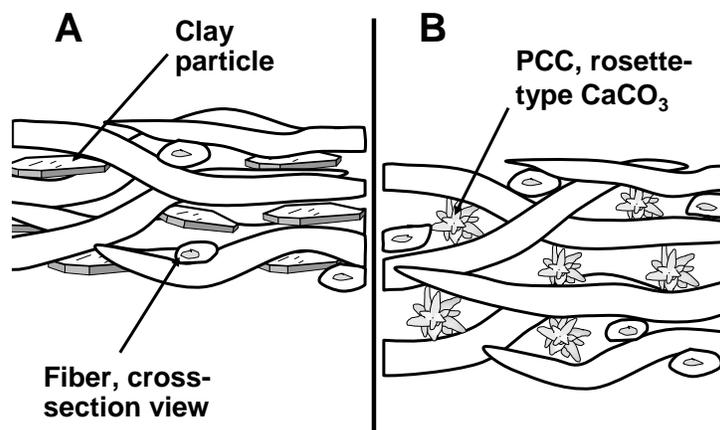


**Fig. 5.** Bracing effect in which filler debonds the paper, but the light scattering is enhanced adjacent to the location of the filler



**Fig. 6.** Covering effect in which the proportion of direct contact between fibers is reduced, but the filler has little effect on paper's density

Based on their own data Beazley and Peterit (1975) concluded that, of the two proposed mechanisms, the “covering” mechanism was the more important. Debonding effects were found to be proportional to the surface area of the fillers that were studied (see also Aaltio 1956; Adams 1993). Less debonding was observed for ground calcium carbonate (GCC) particles, compared to clay, despite the fact that the irregularly shaped GCC particles would be expected to act as more effective “braces.”



**Fig. 7.** Contrasting effects on paper's apparent density, depending on whether the shape of the fillers does (A) or does not (B) allow tight packing

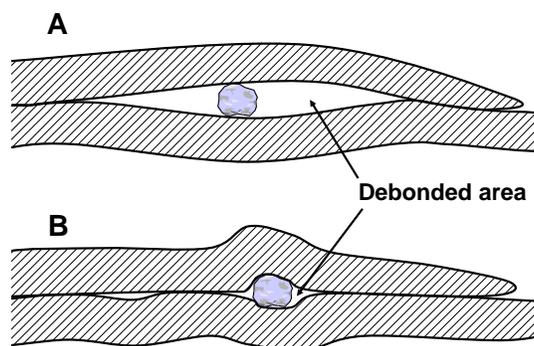
Evidence supporting the “bracing” mechanism includes the known effects of composite-type fillers such as scalenohedral PCC and calcined clay. As illustrated in Fig. 7, the structure of these products would seem to be ideal for the role of holding open spaces between cellulosic surfaces as paper is dried. In addition, these types of fillers have become well known for their greater light scattering ability, relative to such products as ground  $\text{CaCO}_3$  and natural hydrous kaolin (Gill and Scott 1987; Gill 1989; Atherton *et al.*

1997). The same fillers also tend to decrease the apparent density of paper and make the sheet more porous (Gill 1990a,b; Bown 1996).

To further support the bracing theory, one of the most imaginative studies to reveal the mechanism by which filler particles affect paper strength involved filler deposition onto a membrane, which was then pressed against a wet paper handsheet (Li *et al.* 2002). After removal of the membrane, a second wet handsheet was then pressed against the first, making a sandwich. After drying, the sheets were evaluated for Z-directional breaking force. It was found that relatively thick filler particles had a greater debonding effect than platy particles, consistent with effects on the debonded area adjacent to filler particles.

A concept closely related to the “bracing” model is the idea that filler particles, especially those of blocky or composite structure, create points of stress concentration within the paper structure (Eklund and Lindström 1991; Salminen *et al.* 1996). In theory, such points might facilitate the initiation of tensile failure.

To help resolve the issue of “covering” *versus* “bracing,” it is worth keeping in mind that results are likely to depend on the degree of conformability of the cellulosic fibers and fibrils in each case. As illustrated in Fig. 8, highly flexible fibers would be expected to fold themselves around intervening particles of filler, leaving relatively little open space adjacent to the particles. By contrast, relatively stiff fibers, if braced apart, might fail to come together effectively at locations adjacent to filler particles. As noted by Bown (1985a), the apparent light scattering coefficient of a given sample of filler depends on the pulp type, freeness, and sheet-forming conditions.



**Fig. 8.** Illustration of why more conformable fibers are less susceptible to the bracing effect

#### *Filling as a mechanism*

As a third possibility, there may be a “filling” mechanism in which filler particles become situated in void areas of the paper where they do not have a significant effect on paper’s structure (Stark and Eichinger 1990). It was proposed that individual filler particles or agglomerates of filler particles might end up in such locations due to the filtration mechanism that may contribute to their retention. In support of this hypothesis, the same authors reported especially low paper strength in cases where the filler particles were individually bonded to fiber surfaces in a semi-random manner, due to opposite charges on the filler and fiber during the process of formation. Though strategies resulting in fillers being situated in void areas between fibers would tend to minimize the adverse effects on strength properties, the same strategies would also tend to minimize filler’s beneficial effects on paper’s opacity and brightness.

### Particle Shape vs. Paper Stiffness

Among the different strength properties that can be measured, stiffness is one of the most important and the most challenging. Simple theory suggests that stiffness ought to be proportional to the in-plane elastic modulus of the paper, multiplied by the thickness raised to the third power. However, as just discussed, filler tends to interfere with inter-fiber bonding, thus lowering the elastic modulus. Another inherent problem, in terms of trying to maintain the stiffness of paper, is that the density of minerals (*e.g.* 2.3 to 4.2 g/cm<sup>3</sup>) tends to be considerably higher than that of cellulosic material (*e.g.* 1.5 g/cm<sup>3</sup>). As a consequence, filler addition often has the effect of lowering paper's stiffness.

Certain fillers, however, are known to perform better than others, with respect to maintaining stiffness at a given filler content in the paper. For instance chalk and large-size scalenohedral PCC appear more favorable for paper stiffness, compared to some fillers such as clay and fine-particle-size varieties of calcium carbonate (Gill 1989). To rationalize such findings, in light of the theory just discussed, it is reasonable to assume that relatively large, three-dimensional filler particles would increase the thickness of the paper, as in the "bracing" mechanism already discussed. At the same time, the lower surface area of relatively large filler particles would tend to minimize the adverse effect of the filler on the relative bonded area within the paper, helping to avoid a precipitous decrease in elastic modulus.

### Optimizing Refining for Filler Optical and Strength Effects

In the case of unfilled paper made from bleached kraft pulp it is easily shown that increased refining yields lower opacity. This effect is consistent with the increasing conformability of the fibers, resulting in reduced air spaces between fibers after the paper has been dried.

The presence of fillers can lead to a very different relationship between refining and opacity. For instance Bown (1981) reported that at a level of 25% or more of PCC in paper, sheets made with well-refined fibers had a higher opacity than those formed from less-refined fibers. In other words, the relative effect of the fillers on optical properties was greater in the case of well-refined fibers. This observation suggests that filler particles can prevent fibrils, extending outward from the surfaces of freshly refined fibers, from coming together during drying in such a way as to eliminate air spaces. By dissolving the PCC with non-aqueous acid, it was shown that filler particles had been associated with the fibrils.

With respect to strength, refining can be one of the papermaker's primary tools for overcoming the debonding effect of fillers. When considering changes in the composition of groundwood-containing, highly calendered papers over a period of years, Breunig (1981) reported a steady rise in the degree of refining along with an accompanying increase in filler content. Since the strength specifications continued to tighten during the same period, it appears that increases in the extent of refining were at least enough to make up for the debonding effects of the higher levels of filler. Tanaka *et al.* (2001) suggested that the effects of refining and filler addition can be approximately equal and opposite, especially with respect to inter-fiber bonding.

To build upon an idea that was introduced earlier in this chapter, there is evidence that paper made from fibers with a relatively low level of refining are especially vulnerable to the debonding effects of fillers (Aaltio 1956). This observation is consistent with the concept of relatively stiff, unfibrillated fibers being unable to make contact with each other in the regions adjacent to filler particles that end up between fibers at crossing points.

### Achieving a “Peppered” Filler Distribution to Enhance Opacity

In applications involving the use of titanium dioxide particles, it can be especially important to avoid a phenomenon called “optical crowding” (Kwoka 1990; Kwoka and Logan 1994). Optical crowding means that the light scattering ability of  $\text{TiO}_2$  is considerably decreased if the particles are grouped together. Such grouping among the  $\text{TiO}_2$  particles allows light to pass directly from one  $\text{TiO}_2$  particle to another without passing through another phase, such as air or a solid having a lower refractive index. Instances of abnormally low opacity of  $\text{TiO}_2$ -containing paper are sometimes blamed on such problems as inadequate dispersion of the  $\text{TiO}_2$ , or the subsequent excessive re-agglomeration of  $\text{TiO}_2$  by coagulants, salts, or retention aids.

Consistent with the avoidance of optical crowding, Alinec (1987a,b) showed that superior optical performance of  $\text{TiO}_2$  could be achieved by procedures resulting in a “peppered” distribution of the mineral over the surfaces of fibers. Figure 9 illustrates such a distribution. As already noted by Haslam and Steele (1936), it is reasonable to expect that a colloidal mechanism of attaching filler particles to a fiber surface will result in substantial amounts clinging to small fibrils extending outward from the fiber surfaces. Alinec’s research involved selective treatment of either the filler particles, the fibers, or both with cationic poly-ethyleneimine (PEI) before combining the slurry components and forming sheets of paper. Best results were achieved when the filler particles and fibers had opposite signs of surface charge before mixing of the ingredients. In the absence of PEI the mineral particles tended to be retained in a more agglomerated form in the paper. In another study it was shown that substantially worse optical performance could be achieved if the  $\text{TiO}_2$  was agglomerated with cationic starch before addition to the papermaking furnish (Alinec and Lepoutre 1981).

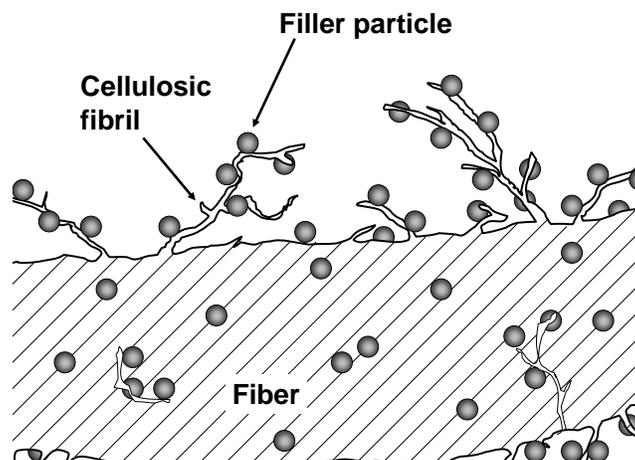


Fig. 9. Illustration of a “peppered” distribution of filler particles on a fibrillated fiber

Another way to avoid optical crowding of TiO<sub>2</sub> involves attaching the small particles in a well-dispersed pattern on the surface of larger filler particles having a lower refractive index. Such a strategy appears to underlie the development of composite fillers composed of kaolin and TiO<sub>2</sub> (House 1993; Curtis and House 1995). The cationic nature of the composite material, due to the cationic polymers, in addition to the relatively large size of the clay platelets, makes it possible to retain the opacifying composite filler with high efficiency.

### **“Extenders” for Use in Combination with TiO<sub>2</sub>**

The term “extenders” is related to a desire, on the part of papermakers, to achieve the high opacity associated with the use of TiO<sub>2</sub>, but to meet the optical specifications with less of that expensive mineral. The idea may have originated with a patent by Olson (1997), involving the combined use of TiO<sub>2</sub> and CaCO<sub>3</sub> fillers. The patent describes mixing of slurries of the two minerals, forming a composite. It was claimed that mixtures containing 50% CaCO<sub>3</sub> achieved opacity gains equivalent to the addition of pure TiO<sub>2</sub>, which when used alone would have been about twice as effective as the CaCO<sub>3</sub>. Though subsequent workers have argued over the reality of such gains (Chang and Scott 1988), the concept of “extenders” has persisted.

Without attempting to support or refute any specific past claims of “unexpectedly high opacity,” let’s assume that there are cases where combined use of TiO<sub>2</sub> and a second mineral product results in light scattering coefficients that are substantially higher than would be predicted by combining results from each type of mineral tested separately in the same furnish and papermaking conditions. One possible way to explain such results is to assume that substantial self-agglomeration of the mineral occurs during the baseline experiments with TiO<sub>2</sub> alone. For instance, one might assume that such agglomeration is brought about when the slurry of mineral particles enters the papermaking system and encounters higher level of water hardness, aluminum ionic species, or various retention aid polymers. It is reasonable to assume that similar agglomeration also occurs during the tests involving two types of mineral products used in combination. However, the expected consequence would be different with respect to the paper’s optical properties; random collisions among the two types of mineral particles would tend to produce a much lower frequency of direct contact between TiO<sub>2</sub> particles, and the overall optical efficiency would be improved due to more changes in refractive index as light passes through the sheet.

### **Apparent Density, Smoothness, and Porosity**

It is hard to discuss paper’s apparent density without also discussing smoothness. A paper product with excess caliper can be calendered to improve its smoothness. But a paper product lacking both caliper and smoothness puts the papermaker in a difficult position. The higher density of mineral, relative to cellulosic material already had been mentioned as an inherent challenge that papermakers face when attempting to maintain caliper at a given basis weight and filler content. According to Bown (1985b), the problem of maintaining caliper is one of the most challenging barriers limiting how much filler can be added to paper, while still meeting property targets at specified basis weights.

Many of the basic strategies for achieving initially bulky, and therefore potentially smoother paper at a given basis weight and filler content follow from points made earlier

in this article. For instance, it has been found that composite-type fillers such as scalenohedral PCC rosettes and calcined clay can minimize the loss in caliper, or even increase caliper in some instances, as the filler level is raised (Gill 1989; Bown 1996; Han and Seo 1997). Although very coarse, blocky filler particles also can contribute to the initial caliper of paper (Han and Seo 1997), the advantage to the papermaker is less clear, since there comes a point where excessively large, non-crushable filler prevent the surface of paper from being calendered to a smooth finish.

The first serious attempt to quantify the incremental effect of fillers on the thickness of paper involved addition of increasing amounts of different mineral products to a fixed amount of fibers, from a master batch (Bown 1983). Tests with uncalendered paper supported a model in which the contribution of filler particles to paper thickness increased in direct proportion to particle size (Gill 1989; Bown 1996). The thickness increment also was found to be proportional to the loss of strength with increasing filler content.

### **Kaolin and Paper's Bulk**

In the case of clay, maintenance of paper's caliper at increased filler levels represents a particular challenge due to the ability of the platy particles to lie down flat on fiber surfaces. In addition, the particles can be expected to align themselves, to some extent, as a result of calendering. The usual result is a denser, less permeable sheet (Adams 1993). Huber and Weigl (1972) envisioned two concepts by which a platy type of filler might, instead, contribute bulk to paper. On the one hand, if particles aligned themselves in a "house-of-cards" structure, a low-density structure would be anticipated. Although such structures are known to exist in aqueous solution, especially in the absence of dispersant (van Olphen 1991), no evidence was found indicating that such structures have enough strength to remain present after the manufacture of paper.

The other concept envisioned by Huber was a "plates and balls" system, a concept that was later demonstrated by Stark *et al.* (1984b). Best effects were achieved with thin delaminated clay platelets. More recently such a system was cited as a way to improve the optical properties of highly filled, highly calendered paper, loaded mainly with kaolin filler (Lorusso and Phipps 1999). Part of the filler should be replaced with "blocky or irregularly shaped" particles according to those authors.

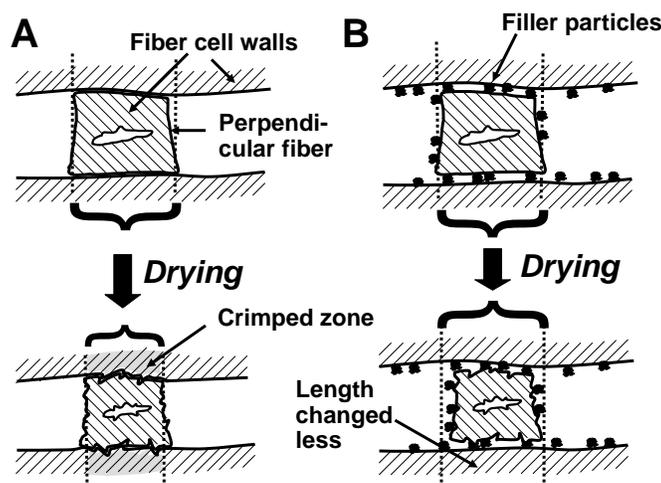
The other main strategy for achieving a bulkier or smoother sheet, opaque sheet using clay, has involved the use of composite-type fillers, such as scalenohedral PCC (Gill 1990; Bown 1996). Before the emergence of scalenohedral PCC as a major papermaking filler, calcined clay filled a similar niche in various paper products (Bauch 1992; Atherton *et al.* 1997). In this respect one composite-type, bulky filler has been displaced by another, less expensive product. In addition to increasing initial bulk, these composite-type fillers also tend to produce more porous and air-permeable paper (Fineman *et al.* 1990), especially when the size of the composite-type particle is increased (Gill 1991). It is interesting to note that large platy talc particles, though they tend to increase the permeability of the wet paper web during the process of dewatering, can have the opposite tendency once the paper is dried and calendered (Biza 1999). Apparently the platy particles are able to align with the paper surface, effectively inhibiting the passage of air through the sheet.

## Dimensional Stability

Various studies have demonstrated increased dimensional stability with increasing levels of filler in paper (Huber and Weigl 1972; Lyne *et al.* 1996). In other words, the paper has less tendency to change its dimensions when subjected to changes in humidity or temperature. Another aspect of dimensional stability involves whether or not the paper will curl, especially if it is exposed to heating on one side. Paper is said to be relatively “dead” if it remains flat under such conditions.

With the exception of the swelling montmorillonite clays and sericite mica mentioned earlier, mineral fillers have relatively little tendency to change their dimensions when exposed to changes in temperature or humidity. Cellulosic fibers, by contrast, are known to swell and contract (Lindström 1986). Despite these facts, it seems that the inherent dimensional stability of most minerals cannot explain the greater dimensional stability of filled papers. One reason to be skeptical about any significant relationship between the dimensional stability of the mineral particles themselves and that of the paper is that the fibers used for filled paper generally tend to be more highly refined, compared to those used for unfilled paper. Increased refining serves as a means of maintaining the needed bonding strength within the sheet. When considered alone, increased refining tends to reduce the dimensional stability of paper (Gallay 1973). Also, filler particles tend to be very small, in comparison with the fibers in paper, and there are almost always wide gaps between adjacent groups of filler particles or individual filler particles in dried paper.

A more likely explanation for filler’s ability to increase the dimensional stability of paper involves a decrease in inter-fiber bonding (Lyne *et al.* 1996). As explained by Page and Tydeman (1962), one of the key mechanisms of dimensional change accompanying the drying of paper is the fact that fibers shrink in their lateral dimensions. Unbonded papermaking fibers shrink upon drying much less in their longitudinal axes, due to the lengthwise predominant alignment of cellulose molecules, as well as microfibrils within the fiber. However, as illustrated in part A of Fig. 10, due to the strong inter-fiber bonding at a crossing point between adjacent fibers, lateral shrinkage may cause crimping.



**Fig. 10.** Schematic illustration of proposed effect of fillers, decreasing the “crimping” effect at the crossing points between fibers

One result of fiber crimping is a reduction in the effective length of a typical fiber in the paper (Nanko and Ohsawa 1989). Part B of the figure presents an idealized model of the effect of filler particles, which are expected to decrease the bonding between fibers. Such interruption of bonding at the crossing points would be expected to allow the paper to maintain its dimensions. There would be less crimping of fibers in comparison to an equivalent unfilled paper sheet. Based on the mechanisms proposed by Page and Tydeman (1962) and Uesaka and Qi (1994), a reduction in dried-in strain would be expected to result in less dimensional change accompanying changes in humidity or temperature.

### **Paper's Coefficient of Friction**

Filler's effects on the frictional characteristics of paper perhaps can be best encapsulated by the words "lubrication" and "tooth." Withiam (1991) presented evidence showing that various porous, high-surface-area fillers, such as synthetic amorphous silicate products, were able to increase paper's coefficient of friction by acting as absorbents for waxy extractives present in and on the fibers. In other words, those fillers were reducing the amounts of lubricating substances available at the paper's outer surface. No correlation was found between smoothness and friction in the cases investigated.

In other cases where wood extractives and other potential lubricants are not the controlling factor with respect to friction, various composite-type and blocky fillers have been found to increase the coefficient of friction (Hoyland and Neill 2001). This observation suggests that the angular "teeth" of mineral edges at the surface of paper could be helping to prevent slippage on various surfaces. This concept is further supported by the fact that platy fillers, able to align with the surface of paper, often tend to reduce paper's coefficient of static or dynamic friction in contact with various substrates (Withiam 1991; Hoyland and Neill 2001).

### **Ink Penetration into Paper**

Two contrasting strategies, both involving fillers, appear to be effective in different grades of paper for reducing the penetration of ink colorants into the interior of a paper sheet (Huber 1970). In the first place, the presence of filler particles can present the fluid with a more challenging, tortuous path through the paper. Especially in the case of paper filled with delaminated clay, the fluid is forced to make its way in tiny channels to get around and between the particles. The result is a high frictional resistance to flow, as can be predicted from the equation of Lucas and Washburn (Eklund and Salminen 1987).

Kent and Lyne (1989) described a related situation in which very fine, spheroidal particles can inhibit the penetration of liquid into paper. In such cases the critical mechanism involves the shape of the meniscus at the leading edge of the penetrating liquid. The liquid front is expected to rapidly enter into the convergent pores formed by round particles at the outer surfaces. However, the liquid front is expected to have difficulty in passing beyond divergent pores at the back sides of the spherical particles, especially in the case of a coated paper product.

Another way in which filler particles can inhibit the penetration of ink vehicle is by absorption. Papermakers make use of this mechanism when porous silica gel particles are coated onto the surface of paper to absorb the colorant from ink-jet formulations, thus

preventing the colorant from penetrating further into the sheet (Koga and Taga 1993). In such cases it is beneficial for the filler or coating mineral product to have a high surface area and internal porosity.

The discussion of liquid penetration would not be complete without at least mention of hydrophobic sizing agents, which often serve as the papermaker's main tool to keep liquids from penetrating paper (Hodgson 1994). Unfortunately, the relatively high surface area of fillers, relative to the lower surface area of dry fibers, means that filler use tends to increase the demand for sizing agents (Gill 1989). The use of bulky fillers, such as scalenohedral PCC, can make it harder to achieve high levels of fluid resistance, especially in cases where the resulting paper has larger pores as a result of the filler, as was illustrated in Fig. 7.

### Minerals for Absorption of Pitch and Stickies

Certain minerals, such as talc, have a remarkable ability to absorb pitch, "stickies," and other tacky or water-hating substances present in the process streams of a paper mill. Talc's ability to act as an absorbent and detackifier has been attributed to its low surface free-energy and platy nature (Lasmarias and Sharma 2003). The relatively large planar size of talc particles allows them to be well retained in paper, thus removing objectionable materials from the process. As mentioned earlier, the added amount of talc needs to be sufficient, *e.g.* 5 to 7.5 kg per tonne of paper, in order to overwhelm the amount of tacky material present (Rooks 1993).

Though many other minerals, such as kaolin clay, cannot match the pitch-absorbing characteristics of talc, their performance in such applications can sometimes be improved by pretreatment. For example, Carter and Hyder (1993) showed that kaolin treated with a highly cationic polymer was more effective for pitch removal, especially when combined with retention aid use. The polymer-treated clay was reported to be more effective than similar products prepared with cationic surfactant, though the latter approach has been advocated by others (Bouffard and Duff 1999). The problem with using surfactant is that such a cationic material can desorb from the mineral surfaces after addition to a process. A related strategy to render clay surfaces cationic, to enhance clay's pitch-retaining ability, involves treatment with an oligomeric aluminum chloride product (Harrison *et al.* 1996).

Other minerals also can become more effective agents for controlling pitch and other contaminants, following their cationization (Hubbe *et al.* 2006). For instance, treatment of zeolite with poly-aluminum chloride, giving it a stable positive charge, has been found effective for absorption and retention of organic materials contributing to the biological oxygen demand (BOD) of wastewater from papermaking operations. Similarly, the pitch-absorbing ability of sodium montmorillonite (bentonite) can be improved by pretreatment with high-charge-density cationic polymer (Derrick 1994; Boardman 1996). Cationic pretreatment also can be applied to talc, helping to improve its retention in paper, in addition to helping pitch removal (Biza 1999).

### Blending of Different Fillers

Given the number of variables involved in the manufacture of paper, selecting the best filler product can be tricky. The optimum filler or combination of fillers will depend

a lot on the type of paper in question (Griggs 1988; Gill and Hagemeyer 1992; Lorusso and Phipps 1999).

In the case of PCC products, one study indicated a possible advantage of combining three parts of ordinary scalenohedral PCC with 1 part of fine-particle PCC having a broad-size distribution (Gill 1988). The combination was found to give a better combination of strength and opacity.

Blends of PCC and GCC have been recommended frequently as a means of achieving a favorable balance of optical properties, strength, ease of sizing, and cost of various grades. For instance, Smith (1999) recommended a combination of 75% PCC and 25% GCC for wood-free paper. Strutz *et al.* (1988) reported better strength and dewatering when 100% PCC was replaced with a blend that contained GCC. In another study, a blend of PCC and GCC was recommended in cases where the papermaker might need to adjust the balance between bulking properties *vs.* strength and runnability (Laufmann *et al.* 2000). In some cases it can make sense to use a higher level of GCC in place of a lower amount of a more expensive PCC, while achieving a fixed set of strength and optical requirements (Davidson 1965; Strutz *et al.* 1991).

One possible approach to making the complex choices among different individual fillers and blends involves calculation of estimated optical properties. For example, Rae (2003) used the Kubelka-Munk theory to predict the effect of combining a low-brightness calcined clay with GCC. Related work was reported by Anderson *et al.* (1988).

## HANDLING OF FILLERS IN THE PAPER MILL

### Dispersion and Stabilization

The issues of mechanical dispersion and chemical stabilization are so important to both the preparation and use of filler materials that these subjects already have been mentioned in some of the foregoing descriptions of filler products. A well-dispersed mineral product is expected to achieve better optical performance, especially in the case of TiO<sub>2</sub> (Bovin and Carnö 1977). Though hot water has been recommended as a way to improve dispersion of clay (Bøhmer 1981), most emphasis has been placed on the use of chemical agents to disperse fillers. Some of the most commonly used dispersants for papermaking fillers are phosphates and polyacrylates (Anderson and Yunko 1983; Stark and Eichinger 1985; Giese 2007), and the mechanisms by which these agents work are well known (Ottewill 1977). Hagemeyer (1984) favored the use of acrylates, rather than phosphates, noting that the latter materials tend to solubilize calcite, gradually making the suspension less stable. Anionic acrylamides have been shown to adsorb exothermically onto filler particles, giving the particles a negative charge and preventing collisions between them (Novak *et al.* 1987a,b; Sanders and Roth 1993). Giese (2007) reported that about 80% of polyacrylate dispersant adsorbed permanently onto the surfaces of calcium carbonate filler. Weigl and Ritter (1995) recommended using trisodium citrate in place of other dispersants in order to minimize adverse reactions with highly cationic polymers being used.

From the papermaker's standpoint, one of the nice aspects about dispersants for fillers is that the supplier of the mineral product usually does most of the work. However,

as mentioned in a review (Rojas and Hubbe 2004), the goals of the mineral supplier and those of the papermaker are not always the same, when it comes to the use of dispersants. The mineral supplier generally will aim to achieve the highest practical level of stability of dispersed material at minimum cost. By contrast, the papermaker always has the concern, at the back of their mind, that excessive dispersing chemicals in the system can make it more difficult to retain fine particles during the formation of paper. Studies have shown that addition of excess dispersant to a mineral slurry actually can hurt its colloidal stability, probably due to the build-up of salt ions (Stark and Eichinger 1985; Sennett 1997), so it is doubly important to avoid adding more than is needed.

### **Retaining Filler During Formation of Paper**

As shown in a classical research article by Haslam and Steele (1936), it is possible to envision three mechanisms by which filler particles can be retained in paper. These might be called filtration, chemical attachment, and mechanical attachment. The filtration mechanism was found to be ineffective, under the conditions of testing used in the cited study. More recent work, as discussed below, shows that filtration can still play an important role when other retention mechanisms are lacking. It was further shown that chemical attachment can be enhanced by such additives as alum and starch. Direct microscopic observations showed filler particles colliding with and sticking to the microfibrils on fiber surfaces exposed to flow. Finally, the authors concluded that a minor fraction of added filler might be “mechanically retained,” mainly by becoming lodged within fiber lumens. Such filler particles could not be removed by repeated washing of the pulp. Though subsequent studies, to be discussed later, have advanced some of these ideas, it is interesting to see that this early piece of work has stood the test of time remarkably well.

### **First-Pass Retention and its Consequences**

The manner and efficiency with which filler is retained in paper can make a big difference in how well the product performs in its end use. As shown by Tanaka *et al.* (1982), a very low level of first-pass retention can yield a very one-sided distribution of filler in paper formed on a single forming fabric. Such distributions are consistent with evidence that the filtration mechanism of retention is inefficient (Solberg and Wågberg 2002), leading to an enrichment of fine particles in the recirculating process water. Two-sidedness also has been observed on commercial-scale Fourdrinier paper machines (Voillot *et al.* 1990; Schlegel and Kilpeläinen 1995; Zeilinger and Klein 1995). Factors that contribute to uneven distributions of filler in the thickness dimension of paper include the filtration mechanism of retention, and also a washing action of stationary dewatering elements, such as hydrofoils and vacuum boxes, in the paper machine forming section (Räisänen *et al.* 1995). The most reliable way to overcome problems of one-sided retention generally involve the optimized use of retention-promoting chemicals.

### **Factors Affecting the Filtration Mechanism**

Under conditions in which filtration is the dominant mechanism of retention, sometimes the efficiency can be improved by increasing the particle size of the filler (Bown 1990). This author demonstrated the importance of particle size by adding a high level of

dispersant, thus eliminating any colloidal attraction between the filler particles and fiber surfaces. Platy particles, such as clay, appear to be retained more easily by filtration, compared to blocky particles having a similar equivalent spherical diameter, based on sedimentation tests (Stark *et al.* 1984a).

The nature of the fiber slurry also can play a major role relative to the ability of the resulting fiber mat to act as a sieve for filler particles. Nevalainen *et al.* (1983) showed that retention efficiency of clay or talc increased with increasing surface area of fibers. The surface area was varied either by changing the nature of the fibers or by adding different levels of fiber fines to the suspension. More flexible fibers yielded denser, less porous wet webs that were more effective in the retention of fillers. Sampson and Turner (1996) reported the curious fact that filler retention became less efficient with increasing solids content of the fiber slurry. They attributed this finding to increased flocculation of the fibers, thus producing a less uniform mat of wet paper that was less effective in filtering the filler particles as water was drained from the mat.

### **Kinetic Aspects of Filler Flocculation and Retention**

The kinetics of flocculation of papermaking fillers and the effects of the polyelectrolyte characteristics on floc properties are also important issues in papermaking. Such aspects have been studied by many research teams (Burgess *et al.* 2000; Fuente *et al.* 2005; Lee and Lee 2006; Modgi *et al.* 2006; Gaudreault *et al.* 2009; Lee *et al.* 2014). It has been shown that the degree of flocculation that can be achieved in a polymer-only system depends strongly on the molecular weight of the polymer, while combinations of polymers and microparticles can significantly increase the degree of flocculation (Burgess *et al.* 2000; Lee *et al.* 2014). It was shown that cationic copolymers with lower charge density yielded larger and less resistant flocs, while cationic copolymers with higher intrinsic viscosity gave rise to smaller and more compact flocs (Rasteiro *et al.* 2010). Smaller and denser flocs were found to provide the most significant improvement in tensile strength of papers (Im *et al.* 2013). The influence of flocculant systems on the structural characteristics of filler flocs was examined by a mass fractal analysis method, and it was shown that the greatest improvement in tensile index can be obtained when highly dense and spherical flocs were formed by this flocculant.

The dynamics of flocculation, deflocculation, and reflocculation of precipitated calcium carbonates (PCC) and clay have been examined using dynamic light scattering and focused beam reflectance measurement (FBRM) techniques (Blanco *et al.* 2002; Yoon and Deng 2004; Rasteiro *et al.* 2008; Lee *et al.* 2014). Rasteiro *et al.* (2008) showed that reflocculation is lower when the flocs are submitted to superficial shearing by sonication than when flocs are submitted to pumping action. Since a single polymer that functions by means of a bridging flocculation mechanism does not give any significant reflocculation capability after shearing (Rasteiro *et al.* 2008, 2010), various approaches have been developed and introduced (Swerin *et al.* 1996; Yoon and Deng 2006a,b; Cheng *et al.* 2011). It has been shown that certain dual-polymer systems improve floc strength and exhibit higher reflocculation capacity than single-polymer systems (Yoon and Deng 2004; Lee *et al.* 2014). Using dual polymers or a polymer with bentonite system for GCC resulted in significant increases in flocculation and reflocculation (Lee *et al.* 2014).

### Strategic Use of Retention Aids for Filled Paper

The subject of retention aid use has been adequately covered in other references (Horn and Linhart 1991; Doiron 1998; Hubbe *et al.* 2009); however, it is worth calling attention to certain retention aid strategies that have been especially applied in the case of filled papers. For example, Carter and Cicerchi (1998) found that they could reduce the requirement for retention aid by splitting the stream of papermaking furnish. The filler was added to just one of the streams of fiber suspension, along with retention aid, after which the streams were recombined. In this way it was not necessary to add enough cationic chemical to overcome the cationic demand of the system as a whole.

Pflieger (1992) noted that two main alternative addition points for fillers, in a typical paper machine system, are the thick stock (*e.g.*, addition to a pulper or machine chest), and just before dilution of the stock (*e.g.*, addition ahead of a fan pump). For purposes of process control it makes sense to be adding at least a fraction of the filler relatively late in the process, thus minimizing process delay before the adjustment results in a change in the product. It is recommended to avoid adding certain filler combinations, such as CaCO<sub>3</sub> and TiO<sub>2</sub>, through the same port, since there can be mutual coagulation and loss of light scattering ability. Pflieger's article also suggests default addition points for a variety of retention aid products.

### Control of Paper's Filler Content

Various types of online sensors and off-line tests have made it possible to control the amount of filler being added to paper. As was noted earlier, there are available methods for determining the filler level by incineration of paper (Anon. 1980; Kocman and Bruno 1996). Related information can be achieved from online measurements of the mineral content or opacity of paper at the reel.

In other situations, the problem may not involve the amount of filler in the product, but rather the efficiency with which filler is being retained. If the retention efficiency varies over time, then both the filler content and other critical sheet properties can vary, making the product less acceptable to the customer. It has become increasingly common to implement online control of retention aid flows, keeping the whitewater solids at a nearly constant level (Rantala *et al.* 1994).

### Strategies to Enhance Filler's Optical Performance

Because papermaking involves huge quantities of fillers, even minor improvements in the efficiency of using these materials sometimes can make a meaningful difference in profitability. This statement is especially true with respect to achieving optical properties. Depending largely on the cost of the fillers being used, papermakers have used basically two kinds of strategies to push the limits of opacity and brightness. This section will consider a set of strategies aimed at maximizing the optical impact of relatively expensive fillers, such as TiO<sub>2</sub>. Later, the final section of the chapter will deal with cases where, due to the low cost of the filler being used, it makes more sense to push the limits of increasing filler content. In such cases the strength of the paper, rather than its optical properties, may tend to be the most critical factor.

*Strategies related to surface charge*

In principle it should be possible to maximize the impact of a set quantity of filler on paper's optical properties by distributing it more evenly over fiber surfaces. Various researchers have pursued the idea of achieving such a distribution by the use of oppositely charged surfaces of fillers and fibers. In one such study it was found that treatment of clay-containing fiber slurries with specific levels of aluminum sulfate (papermaker's alum) resulted in superior retention (Iwanow and Ljadowan 1970). The results suggest that the alum, under those optimum conditions of use, reversed the charge of the clay and caused it to be attracted to the fiber surfaces. Such a mechanism of retention was found to be especially effective in the case of the smallest fraction of clay particles studied, consistent with a greater ability of tiny particles to resist later detachment by hydrodynamic shear (Hubbe 1985). Bown (1990) later reported a similar observation, noting that a charge-neutralization strategy appeared quite effective for retaining very small clay particles, but the same strategy was not effective in the case of larger particles. The surface charge of minerals also can be manipulated by the addition of high-charge cationic polymers during the papermaking process (Alinec and van de Ven 2002).

Alinec (1979) carried out a variety of studies, all pointing to advantages of using positively charged filler materials. For instance, cationic latex was prepared in the absence of an emulsifier. Micrographs of fiber surfaces showed that the latex became deposited on the cellulosic surfaces in a "peppered" distribution when the pH was high enough to render the fiber surfaces negative in charge. Similar effects were achieved with positively charged alumina particles. The principle of depositing positively charged mineral particles onto negatively charged fiber surfaces worked with such high efficiency that it could be used as a way to quantify the external surface area of fibers (Middleton and Scallan 1994). It is worth noting, however, that in Alinec's work (1979) the particles were not firmly attached, and they were able to be dislodged from the fiber surfaces by moderate levels of stirring. In particular, agglomerates of latex did not stay attached, presumably due to their higher vulnerability to hydrodynamic forces, compared to the smaller, individual particles. In summary, although charge-based strategies initially appear to have some promise, there are some practical issues that would tend to frustrate papermakers from attempt to rely too heavily on such an approach. Another way to view the situation is that papermakers are probably throwing away money if they don't attempt to take advantage of the initial surface charge characteristics of mineral products.

**Factors Affecting the Surface Charge of Fillers**

Taking a step back, let's suppose that one of the first goals in optimizing the performance of fillers, with respect to retention and paper properties, ought to be the reliable control of surface charge and zeta potential. The latter quantity is defined as the electrical potential in the solution adjacent to the suspended material, at a location known as the hydrodynamic slip plane (Burns 2002). The slip plane is defined as the position beyond which an individual ion acts as if it is part of the fluid phase, rather than acting as if it were attached to the surface. A strong correlation has been found between the zeta potential values of fillers and such parameters as the specific volumes of given quantities of sedimented mineral particles and viscosities of mineral suspensions (Huber and Weigl 1972).

Jaycock and Pearson (1975) showed that one of the ways to manipulate the zeta potentials of fiber and filler surfaces is by adjusting the pH. In the case of pure mineral particles, it was possible to adjust the pH so that mineral particles such as TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> had zeta potentials that were opposite in sign to that of cellulosic fibers. The effects of pH on zeta potentials were consistent with theory (Ottewill 1977). There was just one problem though. After such mineral particles were exposed to water that had been in contact with the fibers, all of the surfaces behaved as if they were composed of the same material. Later work indicated that the effect was probably due to adsorption of wood-derived colloidal materials onto the mineral surfaces, thus rendering their original zeta potential properties almost irrelevant (Jaycock *et al.* 1976).

Control of the zeta potential of calcium carbonate particles tends to be more complicated, since the mechanism of charging appears to involve the ratio between calcium cations and either bicarbonate or carbonate anions (Dunlop-Jones and Jaycock 1981; Pierre *et al.* 1990). In principle it is possible to make the zeta potential of pure calcium carbonate more positive (or less negative) by adding something like CaCl<sub>2</sub> to the suspending medium. In practice, the concentrations of both Ca<sup>2+</sup> and bicarbonate ions would be affected by such factors as the pH, the hardness of the fresh water being used, and interaction with CO<sub>2</sub> gas from the air. In addition, commercial-grade fillers often contain phosphate or polyacrylate dispersant, which tend to impart a negative zeta potential. A study by Bown (1992) showed that CaCO<sub>3</sub> prepared without any dispersant was retained at higher efficiency than the same kind of filler dispersed with either a cationic or an anionic dispersing agent. Other filler materials having a cationic charge, at least in the absence of dispersants, include calcium sulfate dehydrate (Gussinyer 1986; Gussinyer and Gussinyer 1999) and aluminum trihydroxide (Öhman *et al.* 1996).

### Chemical Treatments to Prepare Cationic Fillers

A more reliable way to give mineral particles a positive charge, with less dependency on ionic conditions, is to treat the system with a high-charge-density cationic polymer (Vanerek *et al.* 2000a,b). For instance, Alinec and Lepoutre (1981) prepared cationic TiO<sub>2</sub> by treatment with polyethyleneimine (PEI). When the cationic TiO<sub>2</sub> was added to a fiber slurry, the resulting paper had relatively high opacity, consistent with a peppered distribution of the mineral over the fiber surfaces. Similar results were achieved with clay filler. However, in that case it was concluded that the particles were not attached strongly enough to the fibers to allow their use in papermaking without separate addition of a retention aid (Alinec and Lepoutre 1983). In follow-up work with TiO<sub>2</sub>, approximately equal retention results were obtained if the PEI was added to the filler, to the fibers, or to the mixture (Alinec 1987a). In another study it was shown that the light scattering efficiency of positively charged TiO<sub>2</sub> particles was improved by increased refining of the fibers, increasing the effective surface area for adsorption (Alinec 1987b). Grenz (1999) demonstrated superior optical performance of TiO<sub>2</sub> in laminate overlay paper if the mineral was “sensitized” by addition of cationic polyvinyl alcohol dispersant, and it is likely that a similar mechanism was involved. Husband *et al.* (1989) claimed a process of combined treatment with both cationic and anionic polyelectrolytes, a strategy which was found to be effective in the case of certain mineral particles that were resistant to stabilization by cationic polyelectrolytes alone.

The idea of pre-charging filler particles was carried out one step further by Stark and Eichinger (1985), who sequentially added oppositely charged filler suspensions to a fiber suspension before making paper. The addition of a dispersion of positive filler particles, followed by negative particles gave the highest retention. Mutual agglomeration of the particles was believed to play a significant role.

Coming back to more practical work, positively charged calcium carbonate products prepared with cationic polymer treatments have been shown to give higher performance during papermaking (Goodwin 1989; Lauzon 1990). For example, Goodwin (1989) reported excellent runnability, overall cost savings, and improved hydrophobic sizing, opacity, and print characteristics. Šutý and Lužáková (1998) showed that it was important in such formulations to use a sufficiently high dosage of cationic polymer to avoid neutralizing and coagulating the suspension. By adding a somewhat higher dosage it was possible to effectively reverse the charge so that the benefits of having a cationic, stable suspension could be achieved. Laufmann *et al.* (1994) described preparation of a related product, using a cationic grinding medium.

### **Filler Pretreatment followed by Retention Aid Addition**

Charge modification usually is not sufficient, by itself, to achieve satisfactory levels of filler retention under realistic papermaking conditions. However, combinations of filler pretreatment, followed by retention aid usage, show greater promise. Carter (1994) showed that pretreatment of filler particles with high-charge cationic polymer improved the efficiency by which an acrylamide-type retention aid was able to retain those particles in highly contaminated furnish, loaded with anionic colloidal material. Retention was low in the absence of the retention aid, despite the initially opposite charges of the filler particles and the other furnish solids. In related work, Mönch *et al.* (1994) showed that though positively charged calcium carbonate has some self-retaining ability, their retention was much more efficient if an anionic retention aid was used before sheet formation.

### **Strategies Related to Retention Aid Uses**

#### *Use of very high molecular weight polymers to retain fillers*

Practical considerations in the selection of cationic or anionic retention aids, as well as the points of addition of various additives affecting the retention of fillers have been outlined by Stark and Eichinger (1985) and by Pflieger (1992). The bottom line, however, is that aside from some subtle differences, conditions of retention aid use that are able to retain filler particles tend to be the same conditions that yield high first-pass retention in general. Part of the explanation for this situation is the previously mentioned tendency for filler particles to become at least partly coated by wood extractives and other anionic colloidal materials present in the furnish (Jaycock *et al.* 1976). A further explanation is that a lot of filler particles become attached to cellulosic fines, and an effective retention aid system may be needed to keep those fines from being washed out of the sheet during the formation of paper. Finally, as noted by Bown (1990), hydrodynamic conditions tend to favor successful capture of filler particles on fibers in the presence of conventional retention aid polymers, due to their very long chain lengths. The relative motion of aqueous solution flowing past fiber surfaces causes the retention aid molecules to become intercepted by fibers or fibrils almost immediately after their addition (Swerin and Ödberg

1997; van de Ven 1989). In subsequent milliseconds of time the protruding tails and loops of polymer can be extremely effective in forming molecular bridging attachments to filler particles. In summary, it is probably fair to say that retention aid polymers usually are applied in ways that give a somewhat indiscriminate effect, causing a haphazard mixture of polymer bridges connecting different solid surfaces in the suspension. In addition, it is probably fair to say that various subtle differences, including the original sign of charge of various filler materials, can potentially become overwhelmed by effects of retention aid polymers subsequently added to the papermaking process. The challenge, then, is to find out if there are more advantageous ways of applying retention aids that can take advantage of filler's surface charge characteristics.

#### *Reverse order of addition - Retention aid before filler*

Though, as just discussed, the conventional order of adding retention aids *after* filler addition tends to work perfectly well for retaining fillers, several studies have reported potential advantages of reversing the order of addition – adding the fillers last. Waech (1983) reported a higher retention efficiency, compared to the conventional order of adding clay and TiO<sub>2</sub> *before* a cationic acrylamide-type retention aid. Likewise, Alinec (1987a) found that cationic acrylamide addition to fiber slurry *before* addition of TiO<sub>2</sub> gave higher retention compared to pretreatment of the mineral with the polymer before addition to the furnish or addition of the same amount of polymer to the mixed furnish. Gruber *et al.* (1996) reported that pretreatment of the fiber with cationic polymer increased the retention of clay, whereas the convention order of addition was much less effective. Ryösö (2001) found such a reverse order of addition tended to be effective only if the delay time between the two steps in the procedure was kept very short.

In light of the findings just discussed, one might ask the question, “why have so few papermakers added high-mass retention aid polymers ahead of filler addition?” The answer appears to be a matter of practicality; the filler often constitutes a significant fraction of the product dry mass, and the papermaking process may tend to run more smoothly if the filler is added early enough in the system so that it becomes very evenly mixed with the furnish long before it reaches the headbox. Retention aids, by contrast, are added in tiny amounts, and their effectiveness tends to be decreased greatly if they have to pass through high-shear unit operations such as fan pumps, hydrocyclones, and pressure screens. So it makes sense to add the retention aids relatively late in the process, just before the formation of the sheet.

To further reinforce the idea of “adding the mineral after the retention aid,” it is worth pointing out that a related practice has become common in a somewhat different context, *i.e.* the case of microparticle retention aid systems. For example, microparticle systems involving sodium montmorillonite (Asselman and Garnier 2001) or colloidal silica (Andersson and Lindgren 1996) are frequently implemented with the polymer being added ahead of the addition point for the mineral. One of the distinguishing characteristics of such microparticle systems is a tendency for enhanced dewatering rates. The distinction between “microparticle” and “filler particle” is further blurred if one considers reports that relatively large particles such as sericite mica (Perng and Wang 2004) or kaolin clay (Hund and Jehn-Rendu 1999) have been found to be effective in the role of dewatering aids, when added to furnish that already has been treated with high-mass cationic retention aid.

## STRATEGIES TO MAINTAIN STRENGTH AT HIGHER FILLER LEVELS

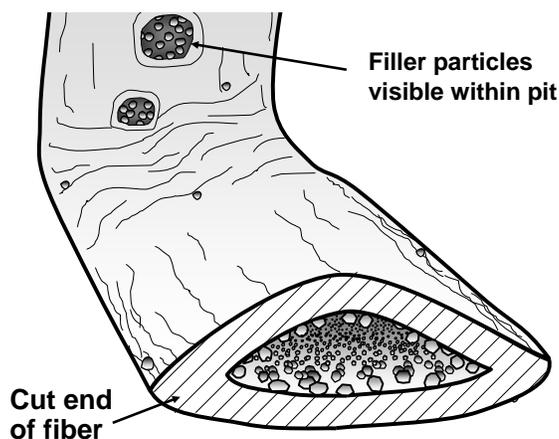
In a typical papermaking operation the delivered cost of calcium carbonate or clay fillers is considerably less than that of bleached kraft fibers. Accordingly, there has been a persistent trend towards higher mineral content in many different grades of paper and paperboard (Breunig 1981; Weigl and Ritter 1995; Krogerus 1999). In the case of printing papers, the average filler content of printing paper has increased at a pace of about 0.2 to 0.3% per year. In Europe the typical filler content of such products increased from about 18% to about 28%, and similar trends were taking place in supercalendered papers (Krogerus 1999). Given such a track record, it is reasonable to expect yet higher levels of filler to become common as time passes.

To get an idea how such ever-higher filler levels will be achieved, the final part of this chapter will consider various “high filler” strategies that already have been successfully demonstrated, at least in the laboratory. The discussion will focus on three topic areas, roughly corresponding to the statements “do something involving the fibers,” “do something involving the filler particles,” and “do something with strength-enhancing chemicals.” The general topic of ways to increase the strength of paper, or to maintain the strength of paper when using less fiber content, has been recently reviewed (Hubbe 2014).

### High-Filler Strategies Focusing on the Fiber

#### *Lumen loading*

A relatively simple strategy to increase filler retention, without the use of chemicals, involves adding the filler to the pulp before the refining operation (Bovin and Carnö 1977; Baker 1999). One of the observed benefits, when using such a practice, is higher strength. An explanation for why co-refining of fibers and filler tends to increase first-pass retention was already provided by Haslam and Steele (1936), who observed that the particles enter into the fiber lumens. The same mechanism was later confirmed by Green *et al.* (1982), and the topic has been reviewed by Kumar *et al.* (2011). The concept of lumen loading is illustrated in Fig. 11, which is based on published micrographs (Green *et al.* 1982; Middleton and Scallan 1985; Rioux *et al.* 1992).



**Fig. 11.** Conceptual drawing of lumen-loaded fiber, showing pits (top), lumen with attached filler particles (bottom), and few filler particles attached to the outer wall. This figure previously appeared in a review article by Kumar *et al.* (2011).

After refining of fibers in the presence of mineral slurry, excess mineral can be washed from the external surfaces of fibers, using a Bauer-McNett classifier (Green *et al.* 1982; Middleton and Scallan 1985; Scallan and Middleton 1985). Paper handsheets are then formed from the slurry. After such preparation, the lumen-loaded mineral is retained at high efficiency, and there is less interference with inter-fiber bonding. Breaking length falls with increasing filler level, but only at about half the rate, compared to conventional addition of TiO<sub>2</sub> to the same furnish. Remarkably, the optical properties are essentially equal to those of control samples having the same overall composition but filled in the conventional way.

One of the most interesting aspects of such research has been the finding that lumen loading of TiO<sub>2</sub> into various types of pulp fibers could be greatly enhanced by pretreating the mineral with aluminum sulfate at a well-controlled addition level (Green *et al.* 1982). Work by Middleton and Scallan (1985) showed that much of the success of the lumen-loading strategy could be attributed to alum's ability to selectively reverse the sign of zeta potential of the mineral surfaces, while leaving the fibers in a negatively charged state. Those authors provided a good description of the theory, explaining how surface charge conditions dictate the success of sticking collisions between surfaces in aqueous suspensions that contain very small particles. The ability of alum to make mineral surfaces positive helps to explain why lumen loading was found to work well only in a pH range between 3.5 and 5.5. More recent work has shown that an oligomeric ionic species of aluminum, the concentration of which depends on pH and concentration, tends to be maximized within that range of pH (Bottero and Fiessinger 1989; Bi *et al.* 2004).

Various work has been carried out to understand the mechanisms involved in lumen loading, and in an effort to make the process work more efficiently. For instance, it has been found that the amounts of TiO<sub>2</sub> depositing within fiber lumens could be fitted to a Langmuir isotherm, consistent with formation of a monolayer of deposited particles (Scallan and Middleton 1985). Such a monolayer coverage was indeed observed in photomicrographs. In micrographs from a more recent study involving lumen-loading of magnetic particles (Rioux *et al.* 1992), a monolayer of such particles is clearly visible through the pit-openings in the fibers. Another interesting finding of that work was the fact that oxidative bleaching tended to have an adverse effect on lumen loading, a finding that is consistent with the tendency of bleaching, when followed by alkaline extraction, to remove negatively charged species from fiber surfaces (Laine 1997). In principle, the lessening of negative charge density at cellulosic surfaces is expected to decrease the attraction between those surfaces and positively charged TiO<sub>2</sub> particles. Follow-up work (Middleton and Scallan 1989) showed that it was possible to essentially "trap" the TiO<sub>2</sub> particles inside lumen-loaded bleached kraft fibers by post-treatment with a cationic acrylamide-type retention aid.

#### *Filling of fiber walls*

An inherent drawback of the lumen-loading strategy just discussed is that the process tends to become less efficient when using types of fillers having particle sizes larger than those of TiO<sub>2</sub>. The pit openings of most fibers from different wood species tend to be too small to allow easy access of the larger filler particles. In theory, one way to get around this limitation would be to add the material in soluble form and then precipitate the

mineral *in situ*, inside of the fiber lumens (Kumar *et al.* 2011). Though such a strategy may make some logical sense, what actually happens as a result of such treatment does not resemble lumen loading. Rather, depending on how it is carried out, *in situ* precipitation usually causes the inorganic solids to end up either attached to the outer surfaces of the fibers or deep within the sub-microscopic pore spaces of the cell wall itself. The latter situation is called “cell-wall filling” or “fiber loading” (Sivén and Manner 2003; Ciobanu *et al.* 2010).

The most significant work related to cell-wall filling has been reported by Allan and coworkers (Allan *et al.* 1992a,b). The resulting pulp was found to give a higher paper strength at a given mineral content. The reported effects were achieved by saturating bleached kraft fibers with sodium carbonate solution, pressing out excess fluid, then diluting the moist mat of saturated fibers with a calcium chloride solution. The diffusion of calcium chloride into the pre-saturated fibers resulted in *in-situ* formation of calcium carbonate, most of which remained in the interior spaces of the cell walls. The authors attributed much of their success in cell-wall filling to their use of never-dried, refined kraft fibers, for which the cell wall pore volume tends to be relatively large, *e.g.* 2 cm<sup>3</sup>/g. Drying of fibers is known to result in semi-permanent closure of pore spaces in the cell walls of fibers (Stone and Scallan 1966; Hubbe *et al.* 2003).

Subsequent work showed that cell-wall-filling can have multiple effects on the papermaking process, in addition to affecting paper properties. Allan *et al.* (1997) observed higher rates of dewatering, following cell-wall filling, compared to the control pulp. Lee (1997) observed that the optical properties of fibers prepared by similar methods exceeded what could be achieved by conventional filling in certain cases. Klungness *et al.* (2000) demonstrated a related system in which fiber slurries were treated with finely divided calcium hydroxide, followed by exposure of the slurries to CO<sub>2</sub> gas within a pressurized refiner. Sheet properties were generally superior to those that could be achieved by conventional filler addition practices. Confirmatory results were reported by Subramanian *et al.* (2005).

Ciobanu *et al.* (2010) compared three different methods of *in-situ* precipitation of calcium carbonate in the presence of bleached kraft fibers, which were then used in preparation of paper sheets having a composition corresponding to printing paper. In all cases, some of the filler was observed to be deposited in the lumen, and some was found to be present within the cell wall.

Silenius (2003), as well as Subramanian *et al.* (2006, 2007, 2008), carried out a series of studies involving similar treatments as just discussed, with the exception that cellulosic fines were employed instead of fibers. The resulting composite fillers made it possible to achieve very high filler loadings while maintaining strength at suitable levels. Sinenius (2003) washed the unattached CaCO<sub>3</sub> particles from the mixture before forming paper sheets. Mohamadzadeh Saghavaz *et al.* (2013) carried out related work by hydrolysis of ammonium carbonate in the presence of calcium chloride and fibrillary fines of kraft pulp.

#### *Other in-situ precipitation strategies*

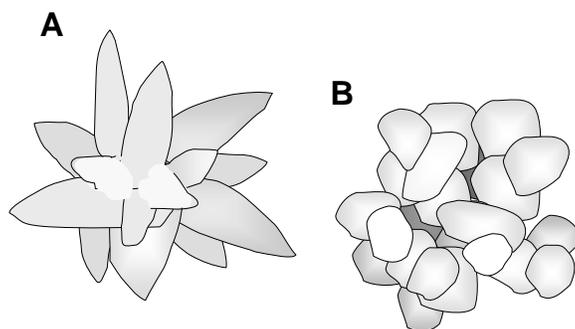
Related studies have been carried out involving strategies which, though superficially similar to the cell-wall-filling technology just discussed, tended to result in

mineral particles clinging to the external surfaces of fibers. Though externally-attached filler particles are less interesting as a high-filler strategy, it makes sense to discuss this kind of research at this point. In early work, Craig (1955) showed advantages of *in-situ* precipitation of calcium silicate in the presence of well-refined pulp. The resulting “fibrous filler” offered high retention efficiency and a strong contribution to light scattering. Hechler (1968) reported *in-situ* precipitation of aluminum meta-hydroxide particles. Though the treatment was found to be beneficial for optical and printing characteristics of the resulting paper, there was a significant adverse effect on paper strength. Results were in general agreement with later related work reported by Bates and Willis (1984). Kumar *et al.* (2009) reported the enhancement of optical properties following in-situ precipitation of calcium carbonate particles onto bagasse pulp.

### High-Filler Strategies Focusing on Doing Something with the Filler

#### *Particle shape innovations for strength*

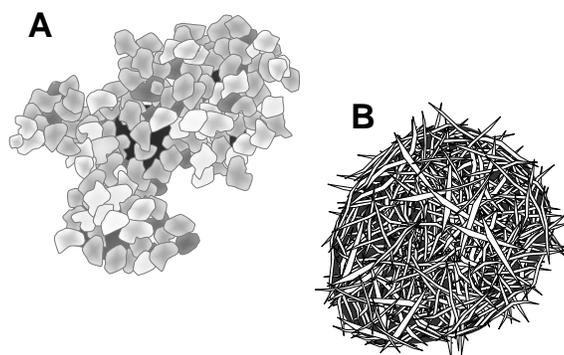
Earlier sections discussed some basic strategies for avoiding excessive strength loss at relatively high filler levels by modifying characteristics of the filler particles. For instance, one main strategy involves increasing the average particle size and decreasing the specific surface area (Beazley and Peterreit 1975). In addition, there have been various unconventional approaches to achieving higher filler levels by modifying the filler’s particle shape or other attributes (Doelle and Amaya 2012). Shen *et al.* (2009b) and Chauhan *et al.* (2011) reviewed work in which inorganic fillers have been modified in various ways to enable higher filler contents while maintaining paper properties. Fairchild (1992) showed that a certain class of composite-type PCC fillers tended to yield a better combination of strength and optical characteristics, especially at relatively high filler loadings. As illustrated in Fig. 12, the so-called “clustered prismatic” PCC particles had blunter points, compared to ordinary scalenohedral PCC. Micrographs suggest that the modification in particle shape would be likely to offer a higher relative bonded area between such products and fibers, compared to other PCC particle shapes having comparable light-scattering ability.



**Fig. 12.** Contrast in shape of (A) scalenohedral PCC vs. (B) clustered prismatic PCC

A related mechanism might also help to explain the superior strength properties that have been achieved with hard, porous urea-formaldehyde filler particles (Menashi *et al.* 1978; Kramer 1993). As illustrated in Fig. 13, item A, those particles have relatively

smooth outer surfaces, lacking angular points that would tend to limit the amount of contact with adjacent cellulosic surfaces. On the other hand, both of these classes of particle have enough texture and porosity so that it is possible to imagine efficient interactions with the flexible microfibrils that extend from the surfaces of papermaking fibers (Clark 1978; McKenzie 1984; Pelton 1993).



**Fig. 13.** Contrast in characteristic shapes of (A) urea-formaldehyde particles vs. (B) high-bulk fibrous calcium silicate particles

Similar considerations also can help to explain very favorable results, in terms of paper strength, that were reported in the case of silicate-based “fibrous fillers” (Mather and Joyce 2004). As depicted in Fig. 13, item B, the particles have a superficial resemblance to loose balls of string. The somewhat parallel alignment of mineral micro-fibers on the particle surfaces, in addition to their spacing, seems likely to be ideal for bonding interactions with the fibrillated surfaces of well refined papermaking fibers.

#### *Filler agglomeration*

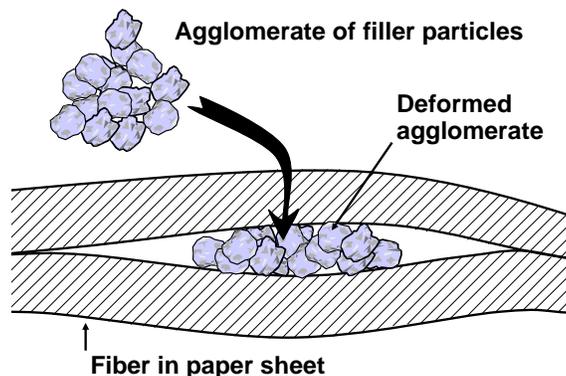
Conventional papermaking practices, especially those involving retention aids, are somewhat indiscriminate in how they affect the state of agglomeration of filler particles in the resulting paper. In principle, a retention aid treatment can form bridges not only between fine particles and fibers, but also among different combinations of fine particles. Gill (1993) reported that ordinary sheets of printing paper exhibit a substantial degree of filler agglomeration, presumably brought about by chemically-induced flocculation. Follow-up work showed that intentional addition of cationic retention aid directly to a stirred suspension of PCC resulted in very strong aggregates that resisted breakup by shear. In principle, such effects can be enhanced by separate agglomeration of filler suspensions before they are added to the fiber suspension (Bown 1985b; Hjelt *et al.* 2008). As noted by Bown (1985b), though such agglomeration tends to hurt the light-scattering performance of fillers (Gill 1993), there is usually an even bigger effect on the paper’s strength characteristics, making it possible in many cases to reach a more favorable combination of strength and/or optical properties at a higher mineral content.

Bown (1985b) reported that one of the most practical ways to pre-agglomerate fillers involves treating an agitated filler slurry with about 0.05 to 0.1% by mass of cationic acrylamide copolymer. Agitation tended to limit the size of the resulting clusters to about

15 to 25  $\mu\text{m}$  (Bobu *et al.* 1986) or 20 to 30  $\mu\text{m}$  (Bown 1985b), though another author cited evidence that yet larger clusters may provide the best overall results (Hayes 1985). Strength benefits of this kind of approach have been demonstrated in a variety of studies (Riddell *et al.* 1976; Breunig 1981; Brooks and Meagher 1982; Hayes 1985; Bobu *et al.* 1986; Stark *et al.* 1984a,b; Stark *et al.* 1987). It is interesting that the treatments involved are essentially similar to the production of “structured clay” products, as discussed earlier in this chapter (see, for instance, Slepetyts and Morgan 1991; Mueller and Brink 1992; House 1993).

A unique way to produce filler agglomerates involves separate preparation of positively and negatively treated slurries of filler, followed by their combination (Seppänen *et al.* 1994). Agglomerates formed in this way were reported to be retained effectively even in the absence of retention aids. In addition to the reported 20 to 50  $\mu\text{m}$  diameters of the clusters, it seems reasonable to expect that the retention benefits might be related to the residual positive and negative areas on different primary particles. Such charged areas would be expected to interact strongly with charged areas of other solids within the suspension. This explanation is consistent with the work of Yu *et al.* (2013), who measured the zeta potential to help understand how treatment of talc with chitosan affected the surface charge.

The usual explanation for strength benefits resulting from filler agglomeration is that there is a reduction in the effective surface area of mineral in the system. Thus, based on the analysis of Beazley and Peterit (1975), one would expect less covering up of potential inter-fiber contact area. In addition, chemically-agglomerated clusters of filler would be soft in comparison to fused mineral clusters of similar size. As illustrated in Fig. 14, the agglomerates would not be expected to be as effective in bracing fiber surfaces apart from each other, compared to rigid composite-type fillers, such as scalenohedral PCC or calcined clay. In addition, the non-abrasive nature of chemically agglomerated suspensions of fine filler particles makes it practical to consider the use of agglomerates that are roughly a factor of ten larger than typical PCC particles.



**Fig. 14.** Illustration of how a deformable agglomerate is expected to minimize the bracing effect

Some other reported benefits of filler agglomeration may be attributed to a reduction in the effective surface area of the mineral additive. Chauhan *et al.* (2013) reported improved hydrophobicity of paper in which the talc filler had been preflocculated with starch. As noted earlier, preflocculation of  $\text{CaCO}_3$  from lime mud was able to

decrease that mineral's adverse effects on hydrophobic sizing efficiency (Peng *et al.* 2014) and strength (Peng *et al.* 2015).

#### *Coflocculation of fillers and fiber fines*

Another variation of filler agglomeration technology involves carrying out the chemical flocculation in the presence of fiber fines (Porubská *et al.* 2002). Gavelin (1985) reported substantial benefits, in terms of retention of either clay, calcium carbonate, or mica, following their coflocculation with cellulosic fines obtained by fractionating bleached chemithermomechanical (BCTMP) pulp. Follow-up work showed that the coflocculation procedure benefited such properties as the drainage rate, opacity, and printing characteristics (Gavelin 1988). Also, the fact that additional retention aid was not needed to retain the filler implies that more uniform, less flocculated paper may be achievable. Similarly, Rahman (1987) reported substantial savings in bentonite dosage when a microparticle treatment was used to coflocculate filler with fiber fines, rather than applying the microparticle treatment to the whole furnish.

#### *Filler agglomeration with cationic starch*

Although the flocculating ability of cationic starch does not match that of high-mass acrylamide products, various studies have shown cationic starch to be effective for agglomeration of fillers. Mather and Jones (1982) showed that pretreatment of clay with cationic starch permitted about a 30% increase in filler content, while maintaining strength characteristics of the resulting paper. Further confirmation of the strength benefits of the same treatment procedures were published (Mabee and Harvey 2000; Mabee 2001). Gerischer *et al.* (1996) reported favorable results from related work in which filler slurries were treated with a combination of cationic starch and an anionic derivative of guar gum. Dosing of the chemicals immediately before sheet preparation gave the best filler retention. More recently, Sang *et al.* (2012) showed the effectiveness of cationic starch as a preflocculating agent to enable the production of highly filled mechanical pulp grades of paper. Yang *et al.* (2013) compared the preflocculating effects of cationic starch and carboxymethylcellulose for filler modification.

#### *Coating of filler particles with dry-strength polymer*

Substantial strength benefits also can be obtained by the cooking of starch in the presence of a PCC dispersion (Zhao *et al.* 2005; Yoon and Deng 2006a,b; Song *et al.* 2009; Fan *et al.* 2012). Such work has been reviewed by Deng *et al.* (2010), who noted a near-doubling of filler content while maintaining strength properties. In the study by Zhao *et al.* (2005) the cooked mixture was dried and then ground with a mortar and pestle, yielding particles with 12% of starch based on the mass of mineral. Thus, each PCC particle or group of particles is coated with its own supply of bonding agent. Shen *et al.* (2010b) reported related work in which precipitated calcium carbonate was coated by the interaction between carboxymethylcellulose (CMC) and aluminum sulfate. Huang *et al.* (2013) treated PCC with a combination of starch, oleic acid, and calcium ions. Gamelas *et al.* (2014) treated calcium carbonate filler particles with cellulose esters and showed paper strength improvements relative to the use of untreated CaCO<sub>3</sub> filler. Chen *et al.* (2014) treated PCC by adsorbing oppositely charged polyelectrolytes - cationically derivatized

chitosan (positive charge) and carboxymethylated chitosan (negative charge). In all of these cited cases, although it is likely that addition of a polysaccharide material at the mineral surface was beneficial to bonding in the resulting paper, it is likely that at least part of the benefits were attributable to filler agglomeration, as discussed earlier. Confirmation of this explanation can be found in the results of Fan *et al.* (2014), who observed the highest paper strength, at a specified filler content, when ground calcium carbonate was prepared with an average agglomerate size of 35 to 54  $\mu\text{m}$ .

### *Surface filling*

The term “surface filling” has been used by some authors to refer to addition of mineral to the paper surface at a size press (Laufmann and Gisella 2011; Shen and Qian 2012). Because the paper already has been formed at that point, none of the mineral is able to interrupt fiber-to-fiber bonding. Laufmann and Gisella (2011) found surprisingly that the filler added to the paper surface became uniformly distributed across the thickness dimension of the paper. Air permeability was decreased, which is consistent with a mechanism in which the mineral occupied spaces that previously had been air-filled.

## **High-Filler Strategies Focusing on Strength-Enhancing Chemicals**

So-called “dry strength agents” have also been considered for production of highly filled paper (Bown 1985b; Baker 1999; Tanaka *et al.* 2001). Some of the commonly used additives include cationic starch, acrylamide copolymers, and guar gum. This final section of the chapter will emphasize some special issues and strategies that have arisen in the context of increased filler levels.

First it is perhaps important to dispel the notion that first-pass retention poses an insurmountable barrier to the amount of filler that can be incorporated into a sheet of paper. Fineman and Lindström (1985) showed, for instance, that a dual-polymer retention aid system was able to achieve filler levels at least up to 50%. Filler levels as high as 80% have been achieved in laboratory studies (Eklund and Lindström 1991), though such practices are not typical for common grades of paper.

Strength and caliper pose the most critical barriers to increased filler levels (Bown 1985b). Briefly stated, two of the key ways that papermakers have attempted to deal with the issue of maintaining caliper (*i.e.* avoiding increases in apparent density) with increased levels of filler have involved the use of bulking fillers and bulky fibers. The space-filling nature of scalenohedral PCC, calcined clay, and to some extent blocky fillers such as chalk already have been covered in earlier parts of this chapter (see, for instance Bown 1996). A more extreme increase in bulk can be achieved by incorporation of plastic “bubble” filler material to the fiber furnish; upon drying the bubbles have been shown to expand, making it possible to achieve increased caliper and smoothness in the calendered paper product (Kenaga 1973). It is also possible to envisage the use of hollow calcium carbonate particles (Enomae and Tsujina 2002), though the feasibility of using such an approach to decrease paper’s apparent density has not been considered. Moberg (1985a,b) provides a useful analysis of opportunities to use bulky chemithermomechanical pulp (CTMP) fibers as part of a strategy for development for highly filled paper grades. The relatively high fiber length

of CTMP fibers, in addition to their space-filling nature, make them good candidates for grades that require contributions to both caliper and strength.

#### *Wet-end starch to achieve high filler content*

One of the most basic strategies that has been used to push the limits with respect to high filler levels has involved cationic starch use at levels that exceed conventional practice (Lindström and Florén 1984, 1987; Lindström *et al.* 1987). Fineman and Lindström (1985) showed that the effectiveness of cationic starch could be greatly increased by sequential addition to the fiber suspension of an anionic acrylamide retention aid. Without such treatment the retention of cationic starch was inefficient, and addition levels higher than about 2.5% starch on fibers, by mass, actually hurt overall retention efficiency. By contrast, with the retention aid it was possible to retain cationic starch with high efficiency, even up to a 5% addition level. By such treatment it was possible to prepare 50%-filled paper having approximately the same physical properties as control sheets prepared with 15% of the same filler.

Advances of anionic starch application technology have made it possible to consider wet-end starch levels as high as 6% (Brouwer 1997; Wielema and Brouwer 2003). The mechanism appears to involve *in situ* formation of polyelectrolyte complexes, between the anionic starch and cationic additives. It would be reasonable to apply such an additive program in the case of a highly filled sheet.

Another way to boost the amount of wet-end starch that can be added to paper is to use a microparticle, as discussed by Kapoor *et al.* (1996). These authors found that a combination of cationic starch and sodium montmorillonite gave higher strength gains, compared to cationic starch alone, making it possible to maintain paper properties at a higher filler level. Khosravani and Rahmaninia (2013) more recently achieved related results with a combination of cationic starch and colloidal silica.

#### *Latex*

Another strategy to compensate for the adverse effect of very high levels of filler on bonding has been to add large quantities of latex binder (Kenaga and Moore 1982; Moore 1982). Latex was found to improve strength properties with increased addition, up to a level of about 5%. Also it was found that the strengthening effects of cationic starch and latex were additive. The combination of latex use, together with a bulky type of calcium carbonate filler made it possible to maintain acceptable sheet bulk and strength with 40% filler content. Post and Fort (1984) claimed a method involving latex addition to the wet end in combination with various other additives. Apparently the mixture showed potential for strength enhancement; however there also was a lot of undesired production of foam and stickies. Beer and Lee (1987) claimed a process in which latex was destabilized with a chemical flocculant in the presence of fibers in order to maximize its effects as a wet-end strength-enhancing additive. Cationic latex also has been found to be effective for highly filled paper, based on lab results (Alinec 2004).

### **Polyelectrolyte Complexes**

Another strategy that has been used to boost strength-enhancement beyond what could be achieved by starch alone has involved oppositely charged combinations of starch

and other polymers. Heath *et al.* (1974) made early progress in this type of system, showing that it is possible to use unmodified starch solutions in combination with various cationic polymers. It is worth noting, however, that these same authors achieved even better results when they simply used cationic starch. Lindström and Florén (1984) were able to maintain strength at high filler levels by combining a high level of cationic starch addition with a high level of anionic acrylamide copolymer. More recent work has helped to demonstrate how polyelectrolyte complexes can form in solution and subsequently be retained on fiber surfaces, where they can act as bonding agents (Hubbe *et al.* 2005). Further work was carried out to understand the mechanism (Lofton *et al.* 2005; Hubbe 2005a) and to define the practical limits of this type of approach (Heermann *et al.* 2006).

## SUMMARY REMARKS

In closing, there is a rich tradition of innovation in the ways that papermakers have used fillers. Mineral filler use in papermaking continues to be a major undertaking, both in terms of its economic impacts and in terms of the properties imparted to paper and paperboard products. In a broad sense, the technologies related to filler use can be regarded as “mature”. However, in numerous areas there have been recent advances in filler technology, and one can expect there to be further innovations in the years to come. Some of the most notable innovations in the past have included developments in precipitated calcium carbonate and in optimizing conditions for usage of higher levels of fillers in various paper grades. There is a continuing need for further research related to achieving a more favorable integration of fillers in the paper sheet, including the uniformity of filler distribution and the association of filler particles with cellulosic fines or microfibrillated cellulose. Opportunities to exploit the favorable attributes of such mineral products as talc, calcium sulfate (gypsum), and aragonite (fibrillary calcium carbonate) deserve research attention. Effects of filler attributes on subsequent operations, such as coating and printing, also are in need of further study. It is hoped that the present “snapshot” of filler technology will help to encourage future efforts in this field.

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