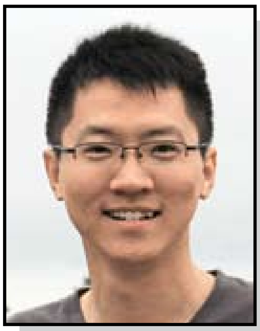
A novel fly ash based calcium silicate paper filler: its retention, drainage and particle size effects

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SUMMARY:

A novel calcium silicate, the byproduct from the value added utilization of fly ash can be used as paper filler, which is known as fly ash based calcium silicate (FACS). Compared to common filler, original FACS has a large particle size (27.6μm), high surface area (121 m2/g) and honeycomb surface. Our previous study has showed that FACS has an advantage in the aspect of paper bulk improvement. In this paper, the wet-end behaviors of FACS with three particle sizes were investigated. The dynamic retention results showed that the filler retention of FACS with three particle size was higher than ground calcium carbonate (GCC) and the retention rate decreased as the particle size decreased without the addition of the retention aid. CPAM can improve the FACS retention remarkably, especially for the filler with small particle size. The drainage test showed that for a given addition, FACS with small particle size exhibited better drainage efficiency in absence of CPAM but the opposite results can be observed when CPAM was adopted. Unlike common fillers, the conductivity of FACS filled pulp was significantly higher than GCC filled pulp and the zeta potential of FACS was lower than GCC filler even though the CPAM was adopted as retention aid.

INTRODUCTION

As the second most used raw material in paper industry, mineral fillers play an important role in improving paper optical properties and printability, saving energy and production cost (1-3). For the past decades, papermakers put great efforts in increasing filler content in paper because the considerable potential in decreasing the cost of paper production. However, higher filler level in pulp furnish or paper can lead to undesirable results, such as lower filler retention and paper strength, thus limiting the filler addition levels in printing and writing paper grades. Therefore, development of new filler or filling technologies becomes an important research area.

Ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), talc and clay are common fillers used in paper industry. Besides, some new engineered filler, such as calcium carbonate whiskers (4), silicate macro-particle filler and silicate nano-fibers (Ben 2005) were also developed, so that the filler content could be increased without compromising paper bulk and strength. Our previous work (5-6) reported a new engineered filler, i.e. fly ash based calcium silicate (FACS), which was produced from aluminum-extracted fly ash in coal-fired power plants. This new filler was verified a good candidate for papermaking since the bulk and strength can be improved noticeably compared to common paper filler. Besides, it can also be used as a adsorbent in the treatment of waste water in paper mill (7-8). Therefore, the development and application of FACS would not only help to release the environmental pressure caused by disposal of fly ash, but also bring some potential economic benefits to coal-fired power plants.

Paper fillers characteristics such as average particle size (APS) and particle size distribution (PSD), specific surface area (SSA), surface charge, brightness and morphology can greatly influence wet-end characteristics and paper properties. Filler particles with large APS and positive charge help filler particles retained in fiber network and alleviate the negative effect on paper strength. Additionally, filler with low specific surface area is good for sizing and paper strength, but can decrease light scattering coefficient. Therefore, there is no filler can satisfy all the properties of wet-end and paper. The selection of filler type for papermaker mainly depends on the paper grades and key properties of paper. For example, FACS filler (5), a large particle size (27.6 μm), high specific surface area (121 m2/g) and porous surface give paper with high bulk and good strength, which can be potentially used in light weighted paper.

In this paper, the wet-end characteristics of FACS with three particle size were evaluated as a further study on the application of FACS in printing/ writing paper grades. The results were compared with those of commonly used GCC filler.

RESULTS AND DISCUSSION

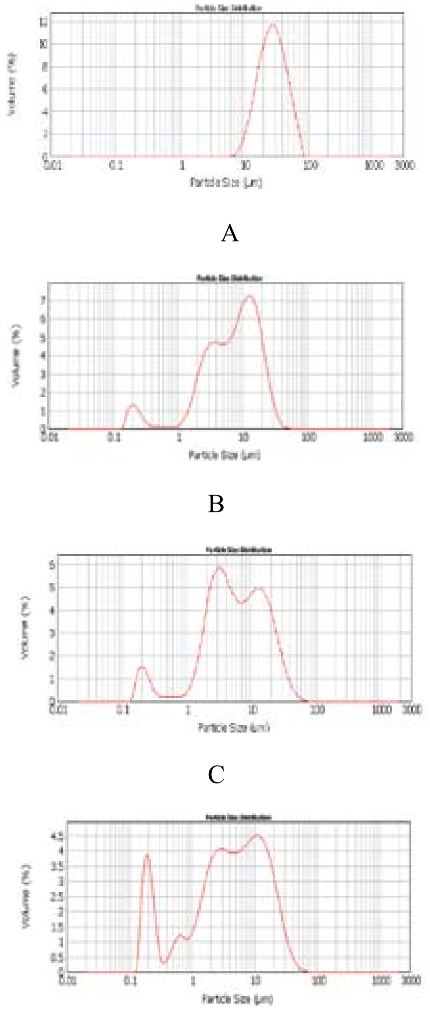
Wet-end characteristics

The characteristics comparison of fillers used in this study are shown in Table 1 and Figure 1. Compared with common filler GCC, original FACS, i.e. FACS0 has a larger particle size and narrow particle size distribution. Filler with large particle size may increase the abrasiveness of forming wire and decrease the optical and surface properties of filled paper (9) but can increase filler retention by mechanical interception. Therefore, we made further efforts to decrease its particle size. As shown in Table 1 and Figure 1, the particle size distribution of FACS increased as the average particle size decreased by ball milling, which help to enhance the packing ability of particles and can be beneficial to paper strength (10) and filler retention by colloid adsorption mechanism.

TABLE 1
Comparison of filler Physical Properties

Filler	APS/μm	PSD*	SSA/ m2·g-1
FACS0	27.6	1.41	121.0
FACS2	8.4	2.35	97.3
FACS3	6.5	3.48	63.4
GCC	4.4	4.30	2.4

PSD*=(d90-d10)/d50,the narrower the distribution, the smaller the PSD



A

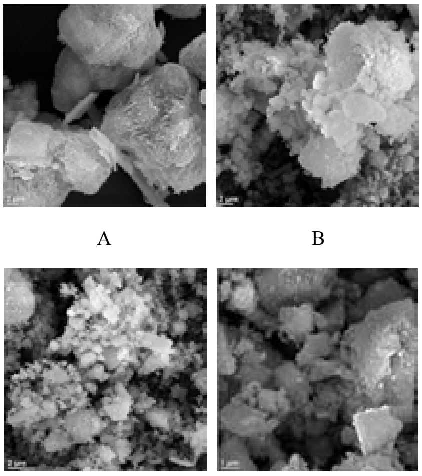
B

C

D

Fig. 1 The particle size distribution of FACS with different average particle size (APS) : (A) FACS0 (B) FACS2 (C) FACS3 (D) GCC.

The noticeably high specific surface area of FACS0 is mainly attributed to its porous surface, as illustrated in Figure 2. The specific surface area of filler theoretically increased with decreasing filler particle size. However, FACS with small particle size showed lower specific surface area. The phenomenon may be caused by two reasons: (a) the thermal energy caused by grinding resulted in the agglomeration of small fragments, and then changed the morphology of particles, which also reported in our previous study. (b) The dry grinding we used may cause the loss of fragments. High specific surface area of filler may help improve filler retention due to their high adsorption on fines and fibers. Grinding process changed the morphologies of FACS, as illustrated in Figure 2. In this process, the porous surface was damaged and the large particles were broke into small particle size. This can explain the increase in particle size distribution of FACS as decreasing particle size.



A B

C D

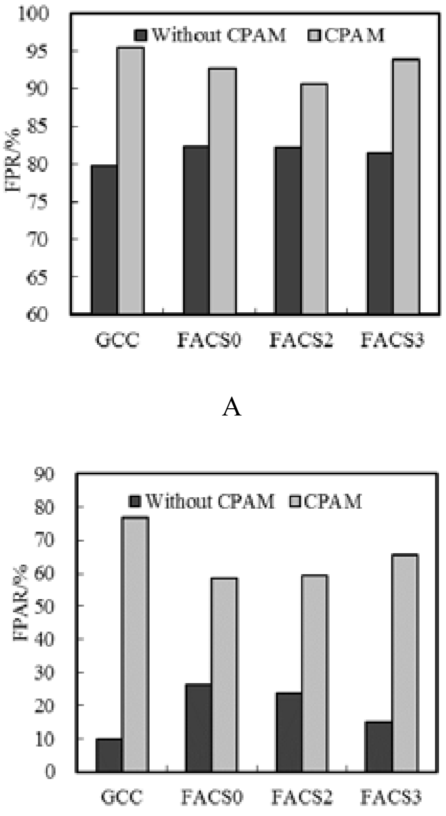
Fig. 2 The morphology of FACS and GCC: (A) FACS0 (B) FACS2 (C) FACS3 (D) GCC

Retention

Filler retention efficiency is crucial to paper production quality, cost and the stability of white water recirculation. As a common and effective retention aid, CPAM was used to evaluate the retention behaviors of fillers in this work. As shown in Fig. 3, the FPR and FPAR of FACS and GCC were improved noticeably when CPAM was incorporated. In the absence of CPAM, FACS retention was slightly better than the GCC retention under otherwise the same conditions. In addition, the FACS retention was decreased as APS decreased. Comparatively, CPAM is more effective for improving the retention of GCC which has a small particle size and board particle size distribution. For FACS fillers, smaller APS also performed better retention behavior when CPAM was applied.

Dynamic retention behaviors of paper filler mainly depend on its adsorption on fines and fibers. Filler characteristics, such as surface charge, specific surface area and particle size, can influence adsorption ability. Figure 4 shows that, in absence of CPAM, the pulp suspension filled with different filler showed similar Zeta potential, which was in the range of -42~-44 mV. However, the conductivity of the pulp exhibited a different way, as shown in Figure 4B. High conductivity of FACS filled pulps is mainly from the dissolving material, such as calcium sulfate which is attributed to the addition of sulfuric acid for decreasing the pH of calcium silicate suspension during FACS production process (11). SO42- and Ca2+ ions in pulp suspension condense the electron double layer and flocculate the FACS particles, thus improving the FACS retention in absence of CPAM. In addition, compared with GCC, FACS fillers had higher specific surface area with in an increasing order of FACS3<FACS2< FACS0, which resulted in the increase of adsorption ability. Therefore, FACS exhibited better retention efficiency compared to GCC filler in absence of CPAM.

GCC and FACS with negative surface charge were readily flocculated with fiber by bridge connection after CPAM addition, which increased the Zeta potential of pulp suspension, thus improving the FPR and FPAR of pulp suspension, as shown in Figure 3 and Figure 4A. Besides, the size and pack ability of the flocs can also impact filler retention. Cheng (12) reported in the presence of CPAM, the filler with smaller particle size exhibited better retention performance compared to the filler with larger particle size. Fillers with small particle size and board particle size distribution are beneficial to the formation of tightly flocs, i.e. increasing the number of filler particles per volume, resulting in the better retention. This explained the better retention obtained by GCC and FACS2 after addition of CPAM. However, the dissolved SO42- and Ca2+ ions from FACS can decrease the charge density of CPAM, causing CPAM molecular chain was coiled and reducing the performance of FACS retention, compared to GCC filler. Therefore, the retention behaviors of FACS mainly depend on its characteristics, retention aids and ion strength in wet-end system



A

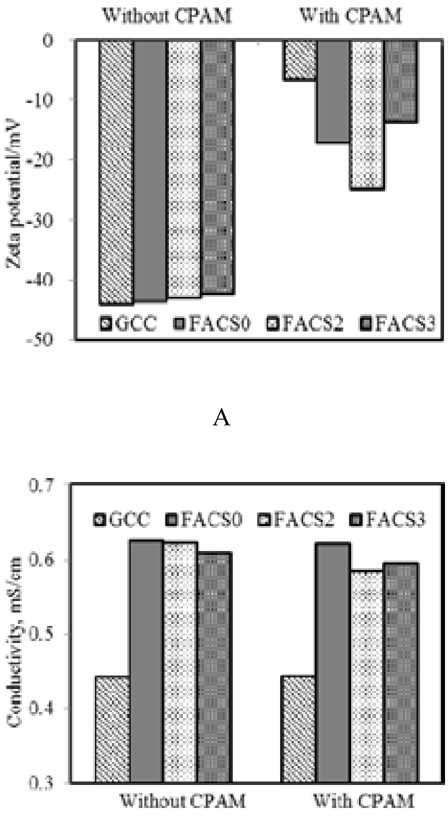
B

Fig. 3 Retention behavior of the pulp suspension added with different filler: (A) FPR (B) FPAR.

Drainage

During drainage test, the stirring speed was fixed at 800 rpm to simulate paper machine speed below 1000 m/min. The effect of CPAM on the drainage performance of FACS0 filled pulp was shown in Figure 4. It can be found that CPAM can effectively improve drainage rate, especially in initial period of drainage. After 40s, the drainage speed became stable. Because of the fluctuation of drainage data, the nonlinear data fitting was adopted ($R^2>0.998$) between 10s and 40s for better investigating the drainage curve of different fillers, as shown in Figure 5.

In the absence of CPAM, the drainage curve of FACS0 filled pulp was similar to the pulp without filler, indicating that the addition of FACS0 had negligible effect on improving the drainage performance by instead of cellulosic fiber, as shown in Figure 6A. In contrast, other fillers, including GCC, FACS2 and FACS3, can increase drainage efficiency in some degree. The drainage efficiency was in decreasing order of GCC>FACS3≈FACS2>FACS0. As illustrated in Figure 6B, for a given drainage time, GCC performed better drainage efficiency. However, FACS filler with larger particle size help to increase the drainage ability of the filled pulp suspension in presence of CPAM, which showed a different behaviors when no retention aid used.



A

B

Fig. 4 Zeta potential and conductivity of the furnish filled with different filler: (A) Zeta potential (B) Conductivity.

Dewatering can be considered as filtration process. During this process, more filtration channels and larger size of filtration channels can increase the filtration efficiency. Therefore, filler type, size, shape and its distribution can affect pulp dewatering process. Filler with high specific surface area, such as FACS0 with 121 m^2/g, increased the specific surface area of the pulp, which increased the contacting chances between water and the filled pulp, resulting in high filtration resistance (13) and low dewatering efficiency, as demonstrated in Figure 5A. In contrast, FACS2 and FACS3 with lower specific surface area showed better dewatering performance. Therefore, decreasing specific surface area facilitates dewatering efficiency in absence of CPAM.

With the use of CPAM, the flocculation of fiber and filler reduced the specific surface area of the filled pulp, and thus improved the dewatering performance. Compared to FACS filler, GCC has the lower specific surface area, and showed the better drainage performance. As stated above, the dissolved ions from FACS weakened CPAM flocculation efficiency. FACS2 filled pulp had the higher conductivity, which may prevent the flocculation between fiber and filler, resulting higher filtration resistance. It is reported that smaller particles in fiber network may block the filtration channels (14) and also increase the filtration resistance. FACS3 had lower specific surface area and conductivity, but its small particle size may raise the risk of blocking the filtration channel in fiber network. The two opposite effects may lead to similar dewatering behavior with FACS2 filled pulp. FACS0 has the largest particle size, the size of flocs formed by CPAM could be larger than other FACS fillers, and thus lead to better dewatering efficiency among FACS filler. Hence, filler particle size, specific surface area and chemical composition can impact dewatering efficiency by changing the characteristics of flocs, such as floc size and packing ability.

CONCLUSIONS

This work mainly focused on the wet-end characteristics of FACS and its particle size on retention and drainage behaviors as an extended study for application of FACS in paper industry. The results showed that differ from GCC, high conductivity of FACS filler resulting from dissolving ions, SO42- and Ca2+ can influence the retention and drainage behaviors. Filler retention was mainly depended on its particle size in absence of CPAM. Original FACS with a high specific surface area and large particle size exhibited better retention. When CPAM was incorporated, FACS filler with small particle size performed better retention

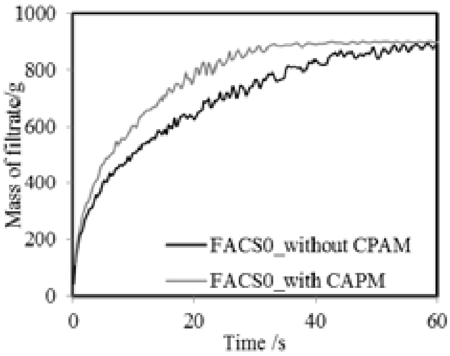


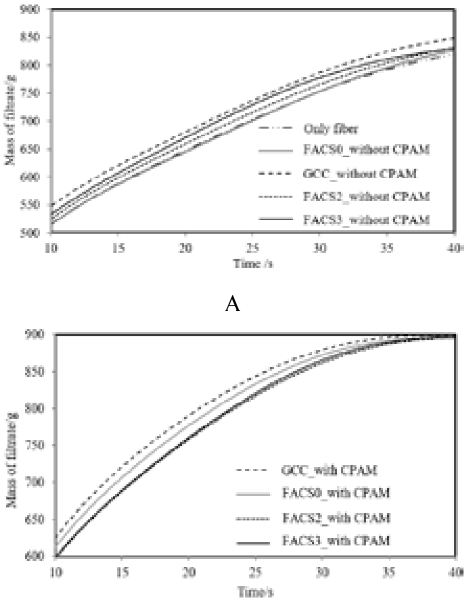
Fig. 5
The drainage curves of FACS filled furnish.

rate because of adsorption effect. In terms of drainage behaviors, FACS with high surface area increased the filtration resistance and thus decreased dewatering efficiency of filled pulp. The decrease of the particle size of FACS helped to improve dewatering in absence of CPAM. When CPAM was employed as retention aid, the FACS filler with small particle size in flocs blocked the channel of filtration and decreased dewatering efficiency whereas original FACS with large particle size was conducive to opening the filtration channel, and thus improving the dewatering efficiency.

EXPERIMENTAL

Materials

The mixed fiber furnish with freeness of 500 mL used in this study consisted of 75% bleached hardwood kraft pulp and 25% commercial bleached softwood kraft pulp. The original FACS (FACS0) filler with average particle size of 27.6 µm was supplied by a coal-fired power (thermal power) plant in China. Its main composition was calcium silicate hydrate. Another FACS fillers (FACS2 and FACS3) with a smaller average particle size than that of FACS0 was prepared by the grinding of the FACS0 using a planetary ball mill PM 100 (Song et al. 2012). The GCC filler was supplied by a paper mill in Shandong province of China. High molecular weight cationic polyacrylamide (CPAM) Percol 182 was provided by BASF.



A

B

Fig. 6 Comparison of the drainage curve of the furnish filled with different filler: (A) without CPAM (B) with CPAM

Filler characterizations

Malvern Mastersizer 2000 was employed to measure the particle size and size distribution of filler. The specific surface area of filler with different particle size was determined using BET method and nitrogen adsorption. The surface morphology of the samples was observed with a JEOL JSM-6400 Scanning Electron Microscope.

Wet-end characteristics

Zeta potential and conductivity of pulp added with filler were tested by Mütek DFR-05 zeta potential apparatus. A dynamic drainage Jar was used to determine the first pass retention (FPR) and the first pass ash retention (FPAR) of the furnish with different fillers. Five gram of 10% filler slurry was added into 400 g of 0.5% pulp suspension, and the furnish was diluted to 500 g with water. The slurry stirring speed was set 750 rpm for 1 min. Next, 0.05% CPAM was added. First 100 ml filtrate was collected after 10 seconds and then filtrated using pre-dried and weighed ashless filter papers. The solid content of residues were determined after drying it at 105^0C. The filler content as determined according to TAPPI Method T211 om-93.

The FPR and FPAR were calculated according to the following equations (Zhang et al. 2009):

$$\text{FPR}(\%)=\frac{\text{Consistency of Stock}-\text{Consistency of DDJ Filtrate}}{\text{Consistency of Stock}}\times 100$$

$$\text{FPAR}(\%)=\frac{\text{Fillers in Stock}(\%)-\text{Fillers in DDJ Filtrate}(\%)}{\text{Fillers in Stock}(\%)}\times 100$$

Mütek DFR-05 apparatus was used to determine the drainage performance of pulp added with filler. 600 g of 0.5% pulp suspension was mixed with 25% filler (based on oven dried fiber), and then was diluted to 1000 g with water. The furnish was then put into the stirring chamber and was homogenized for 10 sec, at a stirrer speed of 700 rpm. Then CPAM was added into the suspension, the stirrer was run for another 10 sec at 800 rpm.

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