Effect of Particle Size Distribution of Lime Sludge on the Hydrophobicity of Paper

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Precipitated calcium carbonate (PCC) is a filler that is widely used for papermaking, and lime sludge is a special type of PCC recovered from the black liquor from kraft pulping. There has been some concern that lime sludge may interfere with the development of paper's hydrophobicity in comparison with commercial PCC and ground calcium carbonate (GCC) due to the presence of impurities when alkyl ketene dimer (AKD) is used as the sizing additive. In this work, fillers with different particle size distributions were prepared, and the effects of particle composition on surface chemistry of fillers, adsorption for AKD, sizing degree of final paper sheets, and retention behavior of fillers were evaluated. The results showed that, through matching different particle size distributions for lime sludge fillers, the negative zeta potential decreased from -26.2 mV to -20.8 mV, the specific surface area decreased from 15.0 m^2/g to 9.1 m^2/g, and total pore volume decreased from 0.037 cm^3/g to 0.026 cm^3/g, which was favorable for the low adsorption for AKD. Consequently the sizing effect of filled paper was improved. Moreover, the retention rate also was increased by changing the particle size distribution of lime sludge.

Keywords: Lime sludge; Calcium carbonate; Particle size distribution (PSD); Sizing; Paper

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INTRODUCTION

Lime sludge is a by-product of recovering alkali from the pulping process. The main chemical component of lime sludge is calcium carbonate; it also contains a small proportion of residual metal compounds and alkali. At present, there are two kinds of lime sludge: one is produced from wood pulp, and the other comes from non-wood pulp (Zhang *et al.* 2005). In general, the lime sludge from wood can regenerate lime after burning and then be recycled in pulp and paper processes. However, the majority of lime sludge coming from non-wood pulp contains silicon and other impurities. Because of undesirable caking behavior, such lime sludge often ends up in landfills (Pan *et al.* 2009).

Inorganic mineral fillers are used along with fibers for the production of paper (Chauhan *et al.* 2011b). They replace a proportion of expensive and scarce fiber material, decrease papermaking costs, and enhance the optical and functional properties of paper. They also decrease the energy demand in the papermaking process due to the use of a smaller mass of water-containing fibers per unit weight of paper (Chauhan *et al.* 2011a). To date, this lime sludge has not been used as a filler in paper alone, because its use causes a drop in paper properties, especially hydrophobic sizing attributes. So some companies only mix post-refining lime sludge and commercial calcium carbonate together for use as paper fillers.

"Sizing" is the process by which a chemical agent provides paper and paperboard with resistance to liquid wetting, penetration, and absorption. Cellulose is a hydrophilic polysaccharide with a high surface energy. The porous structure of paper acts like a sponge in the presence of liquid. The purpose of internal sizing agents is to make cellulosic fibers hydrophobic and thus control the wettability of paper and the operation of paper machines. The sizing process comprises retention, distribution, spreading, and anchoring of the sizing agent to fibers (Hubbe 2007). The most widely used neutral/alkaline sizing agents are alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). In fact, both ASA and AKD are considered effective and have been used under neutral/alkaline conditions in papermaking for many years (Sharma *et al.* 2010; Hodgson 1994; Shen *et al.* 2001; Truong *et al.* 2003).

In general, difficulty in achieving satisfactory hydrophobic sizing is a common problem when using calcium carbonate filler in the papermaking process, but the specific mechanism is difficult to affirm. In general, fillers have a large surface area that can consume the sizing agent, and they themselves are not sized, as it is believed that reactive sizes do not react with fillers (Lindström *et al.* 2008). The overall effect is to ultimately reduce the hydrophobicity in paper (Krogerus 2008). In one study (Karademir 2002), the impact of calcium carbonate on hydrophobicity was primarily attributed to the larger specific surface area of calcium carbonate compared to plant fiber material, and this difference led to the absorbance of more AKD on the mineral and reduced the retention of AKD on fibers; however, AKD retained on the fibers contributed the most to the final hydrophobicity of the paper. Moyers and co-workers used calcium carbonate in AKD sizing process and reported that the portion of AKD that coats the calcium carbonate particles gives only a temporary sizing effect (Moyers 1991). Another study indicated that AKD absorbed by fillers was hydrolyzed in the series of paper forming processes and did not contribute to the hydrophobicity of paper (Karademir *et al.* 2005). Bartz thought that AKD would migrate and occlude within the porous structure of calcium carbonate when paper was drying, thus decreasing the sizing efficiency (Bartz *et al.* 1994). Furthermore, lime sludge can give rise to a larger negative impact on AKD sizing than commercial calcium carbonate because of its lower purity, non-uniform size distribution, and looser pore structure. Some authors have reported the effect of the particle size of talc filler on the physical properties of paper, and the hydrophobicity of talc filled sheets was reduced on loading of lower particle size (Chauhan *et al.* 2012, 2013). Bartz showed that the sizing efficiency of PCC filled paper was improved with larger particles, because their smaller pore surface areas rendered more AKD available (Bartz *et al.* 1994). It has also been reported that the filler weakened the paper by decreasing the inter-fiber bonding; this effect increased with the decreasing filler particle size (Fairchild 1992; Adams 1993; Han and Seo 1997; Krogerus 1999; Kinoshita *et al.* 2000). However, there has been a lack of research on the effect of particle composition on the surface chemistry of fillers, as well as on sizing degree of the filled paper sheet.

Thus, the present work attempts to provide some information on the effect of particle size distribution on physico-chemical properties of lime sludge, their adsorption for AKD, and the hydrophobicity of filled paper. Meanwhile, as a comparison, the influences of particle size distribution on sizing property of commercial precipitated calcium carbonate and ground calcium carbonate were assessed as well.

EXPERIMENTAL

Materials

Lime sludge, PCC, GCC, chemithermomechanical pulp, reed pulp, bleached sulfate softwood pulp, cationic starch, AKD latex, cationic polyacrylamide (CPAM), and bentonite were all supplied by Yueyang paper mill (Yueyang, China). The furnish was 50% of chemithermomechanical pulp, 30% of reed, and 20% of softwood pulp.

Methods

Filler gradation

Lime sludge, PCC, and GCC were graded through screening and centrifuging Filler samples with various particle size distribution were obtained, and the particle size distribution (PSD) was determined with LA-950 HORIBA laser particle analyzer (made in Japan), the results were shown in Table 1(1-a, 1-b).

Table 1-a. PSD of Lime Sludge and PCC after Grading

Kinds of fillers		＜2 (μm)	＜5 (μm)	＜10 (μm)	Average particle size (μm)
Lime sludge	1	13%	99.5%	100%	2.6389
	2	5%	48%	98.6%	5.1626
	3	6.9%	32.5%	92.3%	5.9148
	4	9%	45%	68.5%	10.6815
	5	8.5%	43%	74%	11.2994
	6	1.6%	31%	59.5%	23.5378
PCC	1	12.3%	15%	99.8%	5.8059
	2	0	2.9%	100%	5.9866
	3	0.8%	5.7%	99.8%	6.4715
	4	5%	26%	85%	6.9687
	5	0	4.5%	99.2%	7.3555
	6	0	11%	98.6%	8.5334

Characteristics of graded fillers

The pH of the filler suspension (0.5%, mass fraction) was measured with a pH meter. The dry filler powder was dissolved in water, and the concentration of the suspension was 0.0001g/mL, which helped in testing the zeta potential with a Malvern Zetasizer Nano analyzer.

Table 1-b. PSD of GCC after Grading

Kinds of fillers		<2 (μm)	<3 (μm)	<5 (μm)	Average particle size (μm)
GCC	1	65%	96%	100%	1.4375
	2	17%	75%	100%	2.2461
	3	24%	90%	100%	2.2620
	4	20%	74%	100%	2.4467
	5	1.08%	18%	100%	3.3098

Fillers were designated as 1, 2, 3, 4, 5, and 6 based on the increasing average particle size.

The specific surface area of the samples was determined using a multipoint BET method with nitrogen as the adsorbate in a Quantasorb Sorption System (Quantachrome). Pore volume analysis was performed on calcium carbonate using an analyzer from Micromeritics ASAP 2020 (USA).

The powder samples lime sludge-5, PCC-4, and GCC-4 were examined under scanning electron microscope (SEM) using the gold shadowing technique to determine the fillers' shape.

AKD adsorption on various fillers

A certain amount of AKD latex was diluted to different concentrations. Then, the absorbance of AKD with different concentrations was tested at 238 nm with an ultraviolet (UV) spectrophotometer (Hach, USA) to draw a normative adsorption curve.

Fillers with different PSD were dispersed with a magnetic stirrer, and then 80 mg AKD/g filler was added to the uniform filler suspension, and stirring was continued for 2.5 min. After mixing, the AKD/filler mixtures were centrifuged by suction filtration, and the supernatant was used to test absorbance using the UV spectrophotometer. The amount of AKD absorbed by the fillers could thus be determined.

The formula for the standard UV concentration curve of AKD was,

$$y = 0.01406x+0.02868 \qquad (1)$$

where, x is the concentration of AKD (μg·mL^{-1}) and y is the absorbancy. The coefficient of determination for the regression fit (R^2) was 0.9997. The curve was showed in Fig. 1.

Handsheet preparation and testing

The order of papermaking was as follows: preparing pulp→cationic starch→AKD→CPAM→lime sludge/PCC/GCC→bentonite→forming. The consistency of stock was 1% (w/v), and the time interval between AKD and fillers was 2.5 min. The dosages of cationic starch, AKD, cationic polyacrylamide, and bentonite were 0.75%, 0.25%, 0.043%, and 0.5% (to oven dry stock dosage) respectively, and that of fillers was 24% (to total paper). Paper handsheets of 70 g/m^2 substance were prepared for testing. The filler retention ratio in paper was determined at 575 °C in a muffle furnace (Shen *et al.* 2008) and was calculated with the following formula,

$$Filler\ \ retention\ ratio(\%) = \frac{\mathrm{A}}{m \times (1-a)} \times 100 \tag{2}$$

$$a = \frac{m_1 - m_2}{m_1} \tag{3}$$

where *A* is the ash remained in the paper (g), *m* is the weight of filler added to the paper (g), and *a* is the mass loss fraction (%), which was calculated based on formula (3), and the filler was burned at 575 °C in a muffle furnace. In Eq. 3, m_1 is the weight of filler without burning, and m_2 is the weight after burning.

The hydrophobicity of paper was measured using the $Cobb_{60}$ value. The $Cobb_{60}$ of the handsheets was measured using a Cobb sizing tester as per TAPPI test method T 441 om98. All experiments were carried out in triplicate, and the bars shown in the figures represent the standard deviation on either side of the mean.

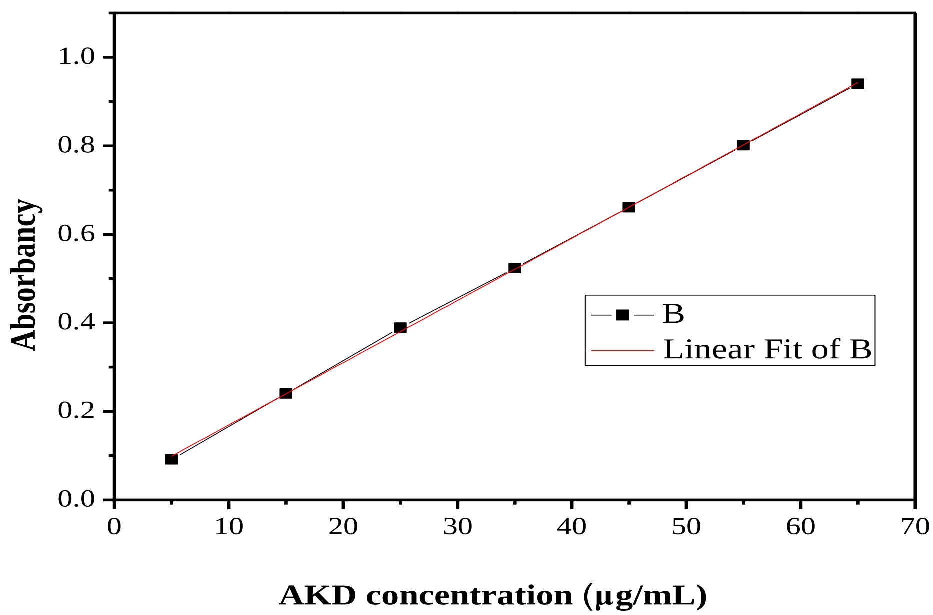

Fig.1. AKD UV normative absorption curve as a function of concentrations

RESULTS AND DISCUSSION

The pH Value and Zeta Potential of Different Fillers

As shown in Table 2, the pH values of these three kinds of fillers were all around 10, indicating an alkaline mineral surface, regardless of their particle size. While the surface electrochemical property of fillers can be altered by various measures that may be used to change the particle size distribution, there was no definite relationship found between particle size distribution and zeta potential of fillers. There was a detectable difference in zeta potential for lime sludge with different particle size distribution, as well as PCC and GCC. The largest difference in zeta potential of lime sludge with various particle size distributions was about 6 mV. Moreover, for PCC fillers, there was a significant difference in their particle size distribution between number 2 with the minimum zeta potential (-10.1 mV) and number 4 with the maximum zeta potential (-17.4 mV), and number 4 exhibited broader range of particle size distribution than number 2, with 97.1% of the particle sizes concentrated within the range 5 to 10 μm. Similar results for GCC are shown in Table 2 and Table 1-b. The negative zeta potential of number 1 was much lower than that of the other samples; it can be noted that its average particle size was relatively small, and much more of the particle size distribution was less than 2 μm, which was distinct from the other samples.

Table 2. The pH and Zeta Potential of Fillers with Different PSD

Kinds of fillers		pH value	Zeta potential (mV)
Lime sludge	1	10.02	-23.76
	2	10.30	-22.55
	3	10.17	-25.3
	4	10.26	-20.8
	5	10.21	-26.2
	6	10.31	-26.1
PCC	1	10.10	-13.56
	2	10.13	-10.10
	3	10.20	-11.4
	4	10.33	-17.4
	5	10.05	-15.78
	6	10.18	-12.04
GCC	1	10.05	-16.28
	2	10.20	-33.7
	3	10.41	-49.97
	4	9.97	-34.97
	5	9.75	-38.3

Specific Surface Area, Pore Size, and Morphology of Fillers

As is well known, the pore size of filler particles has an important impact on its adsorption capability for fiber fines and paper chemicals. At the same time, the morphology of fillers mainly influences their retention on fiber mat. As shown in Fig. 2, the PCC particles exhibited a typical spindle-like shape; GCC was in the form of thin sheets, while the lime sludge consisted of aggregated sheets. Table 3 shows BET surface areas and pore sizes of the fillers. As expected, the BET surface area basically decreased along with the increasing of average particle size for all three kinds of fillers. In the meantime, the BET surface area of lime sludge was much higher than that of the PCC and GCC, despite the fact that the average particle size of lime sludge was much larger than GCC. The possible reason was the bigger total pore volume and irregular morphology of lime sludge. For lime sludge, matching the particle size produced significant difference in specific surface area from about 15 m^2/g to 9 m^2/g; For GCC, the specific surface area changed from about 7 m^2/g to about 3 m^2/g, and accordingly the total pore volume from 0.0186 cm^3/g to 0.0079 cm^3/g.

Table 3. Specific Surface Area and Pore Diameter of Fillers

Kinds of fillers		BET surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
Lime sludge	1	15.0238	11.0564	0.0368
	2	13.7465	10.1121	0.0348
	3	12.2115	11.0152	0.0336
	4	10.4036	11.4669	0.0261
	5	9.8729	11.5679	0.0259
	6	9.0977	11.3415	0.0295
PCC	1	4.2346	9.0245	0.0078
	2	3.0812	8.8116	0.0068
	3	3.5481	8.2303	0.0073
	4	2.9124	8.8181	0.0064
	5	2.9736	7.8877	0.0059
	6	3.9912	8.8618	0.0088
GCC	1	6.6765	11.1680	0.0186
	2	4.2528	11.0894	0.0118
	3	4.7896	11.8614	0.0142
	4	4.4567	11.6734	0.0124
	5	3.0136	10.4313	0.0079

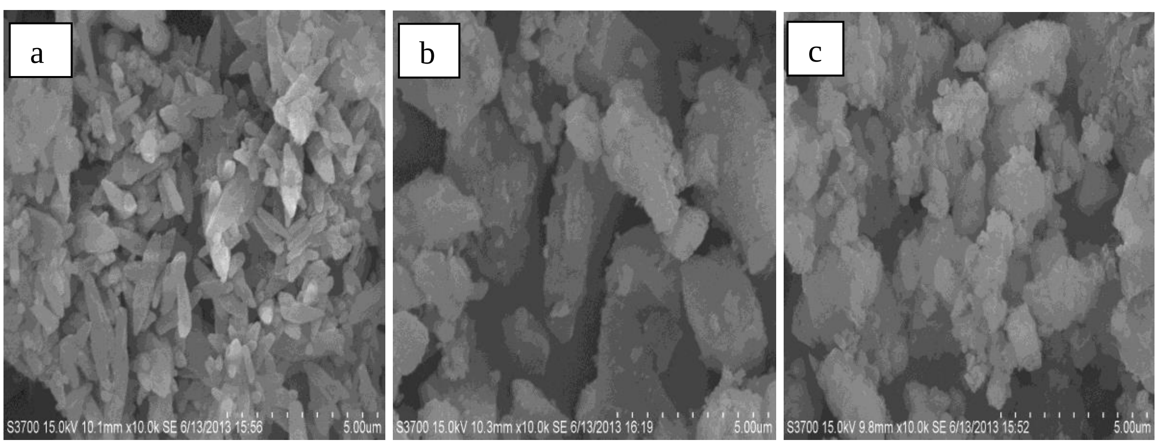

Fig. 2. SEM images of fillers (×10000) (a: PCC; b: GCC; c: lime sludge)

The Adsorption of AKD on Fillers

Based on the results shown in Table 2, the three kinds of fillers were negatively charged. Since both the fillers and the fiber have a negative charge, their surfaces compete for adsorption of the stabilized AKD particles. This competition results in a lower sizing degree of final filled paper sheet. Besides the attraction with opposite electric charges, the adsorption capacity was enhanced by the large specific surface area of fillers, as shown in Table 3. As is seen in Fig. 3, the adsorption capacity for AKD of lime sludge was similar to GCC, but was much higher than that of PCC. In general, the total pore volume of both lime sludge and GCC was much higher than PCC; moreover, the negative zeta potential of lime sludge and GCC was much higher than PCC, both of which contributed to the much higher adsorption amount of AKD on lime sludge and

GCC than that of PCC. Some studies have suggested that the AKD absorbed by fillers only makes a temporary contribution to the hydrophobicity of paper (Moyers 1991), and the hydrophobicity of paper was mostly provided by the reacted AKD with fiber. So some solutions to reducing the amount of AKD absorbed by fillers will help to improve AKD efficiency in filled paper.

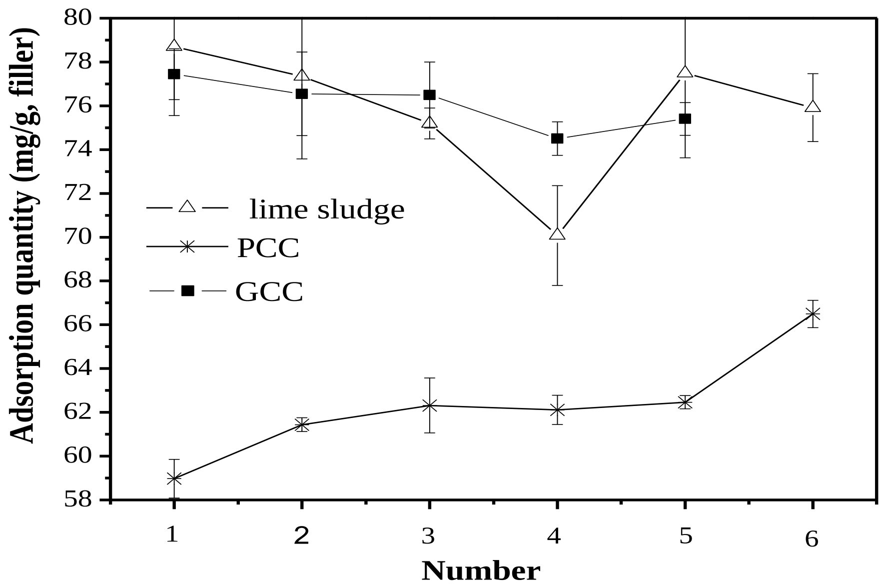

Fig. 3. AKD adsorption on fillers with different particle size distribution

Sizing Property of Paper with Three Fillers

There is a negative effect on sizing properties as mineral fillers are used in paper prepared from cellulosic fibers, and this is also shown in Fig. 4. However, until now, no specific mechanism has been proposed to explain the phenomenon. The higher the Cobb value is, the lower the sizing degree of the paper sheet is. According to Fig. 4, the Cobb value of lime sludge and GCC was 3 to 4 times as high as that of PCC, showing a much poorer paper hydrophobicity of the former than the latter, which was consistent with their adsorption ability for AKD. Especially for lime sludge, the lowest adsorption of AKD (number 4) corresponded to the best sizing effect. In Table 3, the total pore volume of lime sludge and GCC was much higher than PCC, which made fillers absorb more AKD in the wet end and made more AKD migrate into the pore structure when paper was drying. At the same time, one study showed that the hydrophobicity of paper mainly depended on the bound AKD with fibers (Lindström *et al.* 1986). So this process would weaken the final hydrophobicity of paper.

Retention Ratio of Three Fillers in Paper

There are two filler retention theories (He 2010): One is colloid adsorption, which states that superfine powder fillers would be retained by the bridging action and flocculation of CPAM and bentonite; the other is physical retention, which states that large fillers would be retained in the paper by mechanical sieving. Regardless of any theory, the particle size distribution of fillers has a very important impact on its retention.

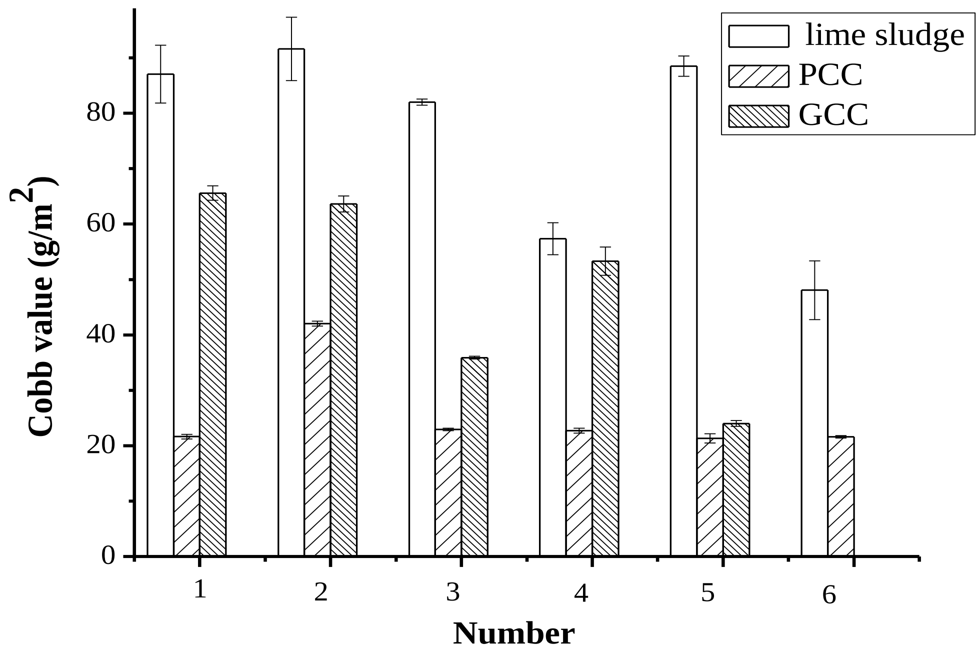

Fig. 4. Cobb value of fillers (the Cobb value was 15.0658g.m^{-2} of paper without filler)

According to the results in Fig. 5, the lowest retention rate was observed for GCC fillers, while all of lime sludge samples showed relatively higher retention rates of over 80%, and the highest retention was for PCC.

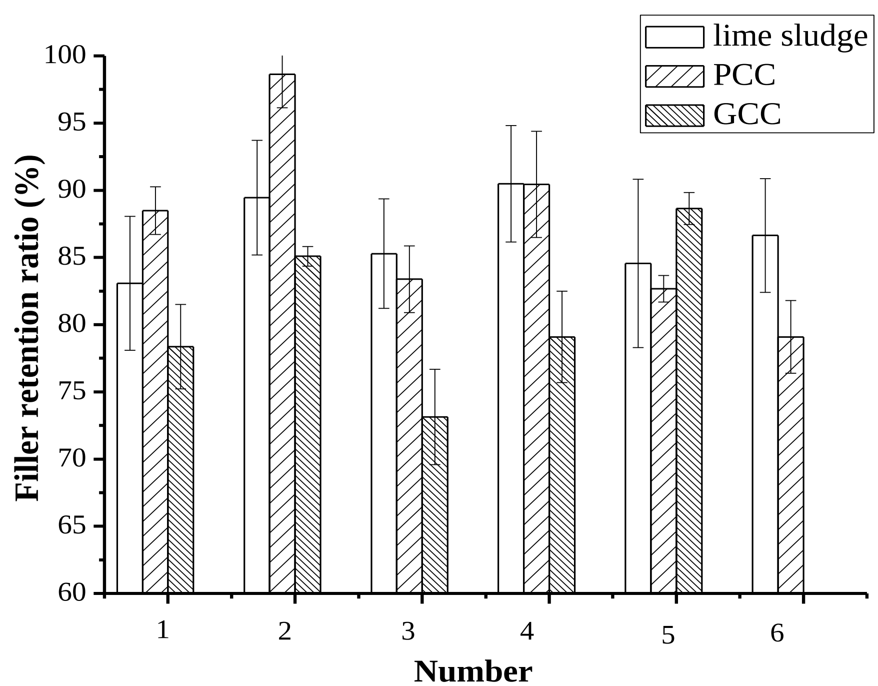

Fig. 5. Retention ratio of fillers in paper

Except for the particle size distribution, the possible reason was the morphology of fillers crystal. Some experts have thought that the sharp ends of PCC particles could combine with the fibrils at fibers surfaces, and then more fillers could be retained in paper. For each kind of fillers, a detectable gap in retention rate was developed between samples with different particle size distributions. For lime sludge, the highest retention rate was 89%, and the lowest was 83%. The difference was just 6%. In the case of PCC, the difference was about 19% between the maximum 98% and the minimum 79%. For GCC, the difference was 15% between 88% and 73% of retention rate, which demonstrated an improved retention performance can be achieved by modifying particle size distribution of fillers. Furthermore, although there was much more filler retained in paper of number 4 than that of other samples in lime sludge series, as was proved by the highest retention rate in Fig. 5, it absorbed the least AKD, thus achieving an improved sizing effect due to the modified particle size distribution.

CONCLUSIONS

1. A modified physical and chemical surface property of fillers including lime sludge, PCC, and GCC was achieved by fitting their particle size distributions. The zeta potential, specific surface area, and total pore volume of fillers were changed significantly, which indicated the potential of managing the particle compositions to lessen their destruction in paper sizing performance.

2. A paper sheet filled with lime sludge with a modified particle size distribution displayed a good sizing effect due to its lower adsorption for AKD sizing agent. Furthermore, a higher retention rate can be achieved by matching the particle size distribution of fillers.

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