Effect of Different Size Ratio and Filling Method on the Characteristics of Calcium Silicate-filled Paper

Sheng Xu, Peng Xu,* Pu-Qi Zhao, and Yu-Ting Du

Process conditions were investigated relative to the use of the fly ash pre-desilication-alkali lime sintering method to extract calcium silicate, which is a by-product of alumina co-production technology, for use as paper filler. The ratio of different fiber raw materials, filler filling ratio, and filling method were studied, and papermaking experiments were conducted. The results showed that calcium silicate filler at a higher proportion (40%) paper can still maintain high mechanical properties. Under the same filling ratio and filling method of calcium silicate filler, the comprehensive performance of softwood pulp and hardwood pulp papermaking paper was found to be better than that of deinked pulp paper.

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Keywords: Calcium silicate; Size ratio; Filling method; Paper properties

*Contact information: College of Textile and Light Industry, Inner Mongolia University of Technology, Hohhot, Inner Mongolia 010080, China; *Corresponding author: xupeng1006@imut.edu.cn*

INTRODUCTION

Fly ash is a fine ash residue discharged from boiler flue gas after pulverized coal combustion. Approximately 80% is flying ash, and approximately 20% is bottom ash (Song 2014). It is a type of artificial volcanic ash. It has strong heterogeneity. Particle components with different morphologies and sizes have different microstructure, phase, chemical composition, and trace element distribution characteristics (Cheng *et al.* 2010).

The world's fly ash emissions are increasing every year, but the utilization rate of fly ash remains at a low level. About 180 million tons of fly ash are discharged annually in China, and the utilization rate is approximately 30% (Sun and Chen 2013). The emission of fly ash from member countries of the European Coal Combustion Products Association is 37.14 million tons, and only 48% of it is used. India emits more than 100 million tons of fly ash annually, with utilization rates below 20% (Wu *et al* 2012).

At present, the comprehensive utilization of fly ash in China mainly focuses on brick burning, road construction, cement and concrete admixture, selection of floating beads, and improvement of soil. Only a small part of fly ash is used in chemical industry and wastewater treatment (Ma *et al* 2020). In the process of comprehensive utilization, there are still some negative effects on the environment, such as dust pollution in ash storage yards and transportation vehicles, treatment of waste residue after extracting useful substances, accumulation of heavy metals in agricultural process, and radioactive problems of building materials products (Hu *et al.* 2011).

The large amount of fly ash occupies valuable land resources, and the heavy metal ions through volatilization and infiltration seriously pollute the atmosphere and water environment, even threatening human health through the food chain (Su and Chen 2009).

Therefore, how to use fly ash reasonably and improve the utilization rate of fly ash has become a hot research topic.

To fully realize the comprehensive utilization of solid waste, Datang International Renewable Resources Development Co., Ltd. uses the high-alumina fly ash resources in the central and western regions of Inner Mongolia; extraction of alumina and the multi-production technology are employed to produce calcium silicate (Yan *et al.* 2012). Its surface is loose and porous, with small true density, high brightness, high coverage rate, and strong affinity with fibers, which meets the basic requirements of paper filler. In addition, the inorganic fillers, such as calcium carbonate and talc powder, which are traditionally used for paper filling, are non-renewable resources. Long-term mining has caused excessive consumption of resources and environmental damage. Using the characteristics of calcium silicate and the auxiliary effect of chemicals, can maximize the content of calcium silicate in paper and achieve the effect of saving energy, fiber, and cost. This paper focuses on the effects of different pulp fiber ratio and different calcium silicate filling methods on paper properties (Xu *et al.* 2017).

EXPERIMENTAL

Materials

In this experiment, bleached sulfate softwood pulp (Arauco BKP, Nueva Aldea, Chile), bleached sulfate mixed hardwood pulp (Aprilasia PT, Pangkalan Kerinci, Indonesia), and mixed waste paper pulp (Yueyang Paper Mill, Tigerlin, Hunan Province, China; ash 8.25%, dust 43.51 mm^2 / m^2) were mixed in different proportions after beating. The chemical reagents of cationic cassava starch (degree of substitution approximately 0.02, Jiangtian brand, Tianjin China), amphoteric polyacrylamide (molecular weight of approximately 200,000, solid content of 15%; Jiangtian brand, Tianjin China), cationic polyacrylamide (molecular weight > 10 million; Sigma-Aldrich, St. Louis, MO, USA), and WPR-350 (Industrial Polyacrylamide Polymers Jiangtian brand, Tianjin China). WPR-350 is a polyacrylamide polymer compound. It acts as an enhancer and retention aid in the experimental process. These items were added in the following order (addition of cationic polyacrylamide, then WPR-350, and lastly cationic cassava starch) according to the experimental requirements. At the same time, calcium silicate filler (China Inner Mongolia Datang International Renewable Resources Development Co., Ltd., Hohhot, China), with its chemical composition shown in Table 1, was added according to the experimental design ratio, and the paper samples were prepared on the standard paper machine for the experiment.

Table 1. Chemical Composition of Calcium Silicate Filler

Component	SiO_2	CaO	MgO	Fe_2O_3	LOI
Content (%)	45 to 47	42 to 45	2 to 3	0.065	7 to 10

LOI: Loss on ignition, the temperature is 650 °C

Experimental Methods

Determination of beating and beating degree

Pulping: A total of 20 g (in papermaking) of softwood pulp and hardwood pulp were prepared, and beating was performed using the Wali Pulping Machine. The consistency of the pulp during beating was approximately 1.57%. First the pulp was beaten lightly, then it underwent hard beating. The beating degree was measured according to the need of beating until the required beating degree was reached (Wang *et al.* 2006).

Determination of beating degree: The beating process was measured by Schopper Riegler Beating and Freeness Tester (IMT-DJD01; International Material Tester, Guangdong, China). When the beating degree of coniferous pulp was 42 ± 1 °SR and the beating degree of hardwood pulp was 38 ± 1 °SR, the beating was stopped and the pulp was removed for subsequent use.

Preparation of paper chemicals

Cationic starch (CS) gelatinization: 5% suspension was dispersed in cold water and stirred evenly, maintained at 90 to 95 °C for 20 min, and then diluted to 1% concentration.

Preparation of cationic polyacrylamide: 13.5% concentration of CPAM was dissolved in water and diluted to 1% concentration for subsequent experiments.

Preparation of WPR-350: A high concentration of WPR-350 was dissolved in water and diluted 20 times.

Preparation of experimental paper

Three groups of experiments were designed. The mixing ratio of coniferous pulp and hardwood pulp in Experiment I was 10:40, the mixing ratio of coniferous pulp and hardwood pulp in Experiment II was 20:30, and the mixing ratio of coniferous pulp and waste paper pulp in Experiment III was 30:35. Calcium silicate filler was added according to 30% and 40% of the mass of mixed pulp. The pulp added with filler was treated by PFI (beating machine) under mixed thaw beating and direct thaw chipmaking. Finally, the experimental results were analyzed.

The required pulp samples were beaten to 38 to 42 °SR according to the ratio of experimental design. The practical conditions of chemical additives were as follows: the dosage of cationic starch reinforcing agent was 1%, cationic polyacrylamide retention aid was 0.02%, and the dosage of the pulp sizing agent alkylketene dimmer (MX-103AKZ, Mingxiang Chemistry Technology Co., Ltd., Shandong, China) was 0.3%. At the same time, the amount of calcium silicate filler was controlled according to the ratio of experimental design, and the paper samples were prepared on the standard paper molding machine. The wet paper was pressed for 5 min and 2 min, respectively, under the condition of 0.4 MPa. Finally, the wet paper was dried on the paper dryer for 5 min, and the handsheet was obtained for the experiment.

RESULTS AND DISCUSSION

Test Results of Calcium Silicate Filler

The samples obtained in experiments I, II, and III were tested after constant temperature and humidity for 24 h. The test results are shown in Tables 2 through 4, and Figs. 1 through 6. PFI Mixed Stirring is the mixing of experimental materials after grinding and beating together. Empty samples are filled only without chemical additives.

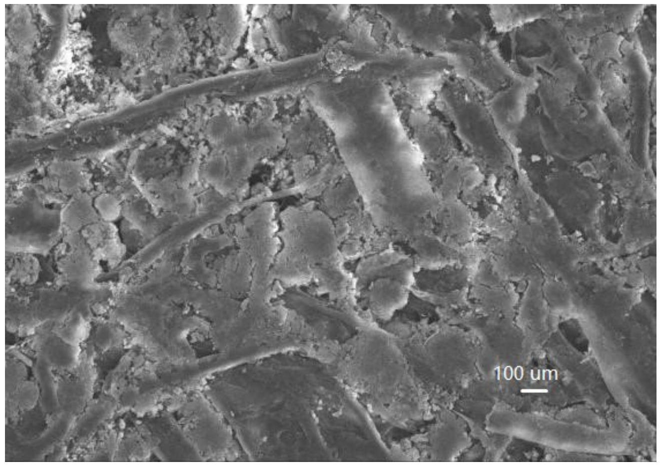

Fig. 1. Experiment I: PFI mixing (30% filler)

Table 2. Experiment I Test Results of Different Calcium Silicate Proportion Filling Paper Samples (Softwood Pulp: Hardwood Pulp = 10:40)

Filler Addition Ratio and Mixing Method	30% Filler (PFI Mixed Stirring)		30% Filler (Mixer Mixing)		40% Filler (PFI Mixed Stirring)		40% Filler (Mixer Mixing)	
Testing Item	Empty Sample (Add only filler but not chemicals)	Add Chemi-cals	Empty Sample	Add Chemicals	Empty Sample	Add Chemicals	Empty Sample	Add Chemicals
Beating Degree (ºSR)	40.5	41.0	41.0	40.5	42.0	42.5	42.0	42.0
Basis weight ($g·m^2$)	62.22	62.70	70.90	76.10	66.48	74.61	65.62	73.66
Paper bulk ($cm^3·g^{-1}$)	2.340	2.381	2.663	2.702	2.505	2.415	2.674	2.675
Brightness (%)	80.57	79.31	80.32	80.66	80.48	79.45	81.14	81.13
Opacity (%)	93.11	95.59	95.03	97.26	95.62	98.43	93.93	95.95
Tensile Index ($N·m·g^{-1}$)	34.10	28.17	26.52	21.99	28.63	22.49	20.40	17.02
Tear Index ($Mn•m^2g^{-1}$)	6.56	6.76	7.75	6.34	6.14	4.88	5.32	4.74
Burst Index ($kPa·m^2·g^{-1}$)	1.65	1.47	1.36	1.16	1.51	1.10	1.20	0.90
Folding Resistance (Times)	9	7	8	4	7	3	2	2
Ash (%)	18.74	22.01	20.59	24.04	22.17	28.30	24.66	28.35

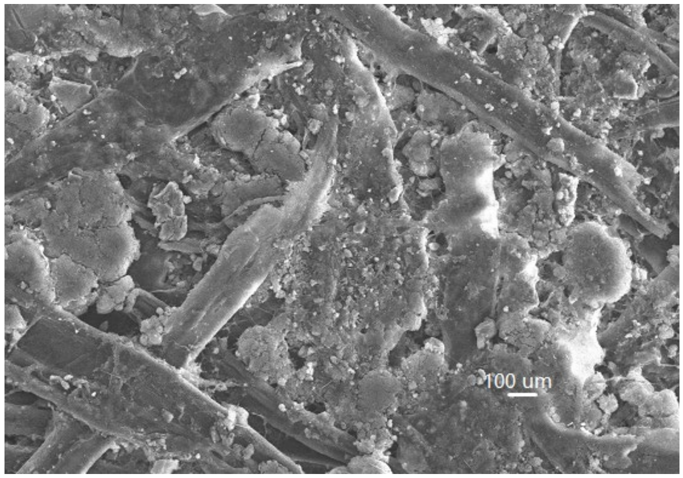

Fig. 2. Experiment I: stirring (30% filler)

Table 3. Experiment II Test Results of Different Calcium Silicate Proportion Filling Paper Samples (Softwood Pulp: Hardwood Pulp = 20:30)

Filler Addition Ratio and Mixing	30% Filler (PFI Mixed Stirring)		30% Filler (Mixer Mixing)		40% Filler (PFI Mixed Stirring)		40% Filler (Mixer Mixing)	
Testing Item	Empty Sample (Add only filler but not chemicals)	Add Chemi-cals	Empty Sample	Add Chemicals	Empty Sample	Add Chemicals	Empty Sample	Add Chemicals
Beating Degree (ºSR)	41	41.5	41	41	42.5	42	42	42.5
Basis weight ($g·m^2$)	64.43	65.54	63.09	63.88	64.83	69.48	63.01	73.5
Paper bulk ($cm^3·g^{-1}$)	2.44	2.45	2.77	2.73	2.49	2.38	2.83	2.79
Brightness (%)	81.19	81.03	81.24	81.43	81.75	81.31	83.18	82.12
Opacity (%)	95.89	94.61	94.62	95.16	94.91	95.85	91.85	95.93
Tensile Index ($N·m·g^{-1}$)	26.88	28.15	23.19	22.38	27.97	22	25.76	19.61
Tear Index ($Mn•m^2g^{-1}$)	7.37	7.06	8.39	7.98	6.72	5.7	7.78	6.46
Burst Index ($kPa·m^2·g^{-1}$)	1.58	1.62	1.38	1.3	1.6	1.36	1.65	1.09
Folding Resistance (Times)	13	16	5	4	8	6	14	6
Ash (%)	19.02	22.67	18.87	23.35	23.41	29.63	25.17	30.29

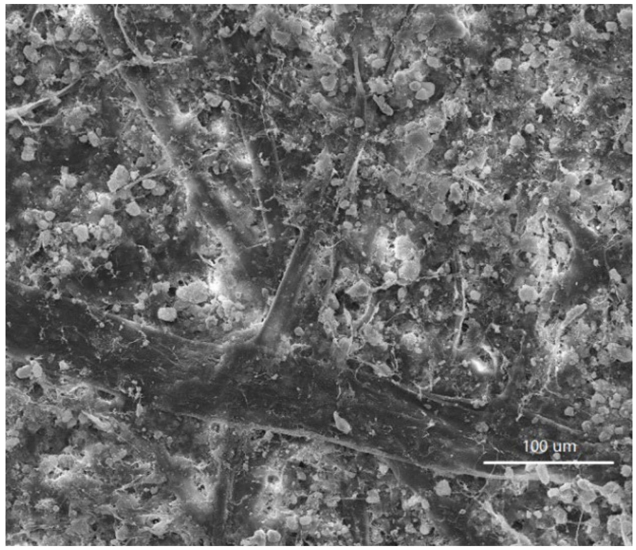

Fig. 3. Experiment II: PFI mixing (30% filler)

Table 4. Experiment III Test Results of Calcium Silicate Filled Paper (30%) (Softwood Pulp: Deinked Pulp = 30:35)

Filler Addition Ratio and Mixing Method	30% Filler (PFI Mixed Stirring)		30% Filler (Mixer Mixing)	
Testing Item	Empty Sample (Add only filler but not chemical additives)	Add Chemicals	Empty Sample	Add Chemicals
Beating Degree (ºSR)	39.5	39.0	40.5	40.0
Basis weight ($g \cdot m^2$)	79.89	80.13	80.65	78.86
Paper bulk ($cm^3 \cdot g^{-1}$)	2.573	2.471	2.479	2.428
Brightness (%)	81.32	81.82	81.21	81.48
Opacity (%)	96.46	96.86	97.38	97.47
Tensile Index ($N \cdot m \cdot g^{-1}$)	21.93	19.12	23.04	21.61
Tear Index ($Mn \bullet m^2 g^{-1}$)	7.56	6.85	8.56	7.84
Burst Index ($kPa \cdot m^2 \cdot g^{-1}$)	1.31	1.37	1.40	1.28
Folding Resistance (Times)	6	7	7	7
Ash (%)	21.07	23.36	30.46	33.23

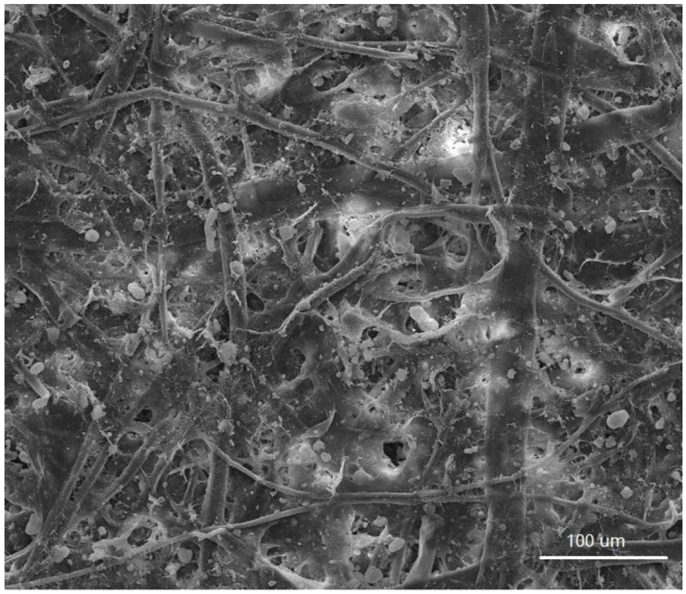

Fig. 4. Experiment II: stirring (30% filler)

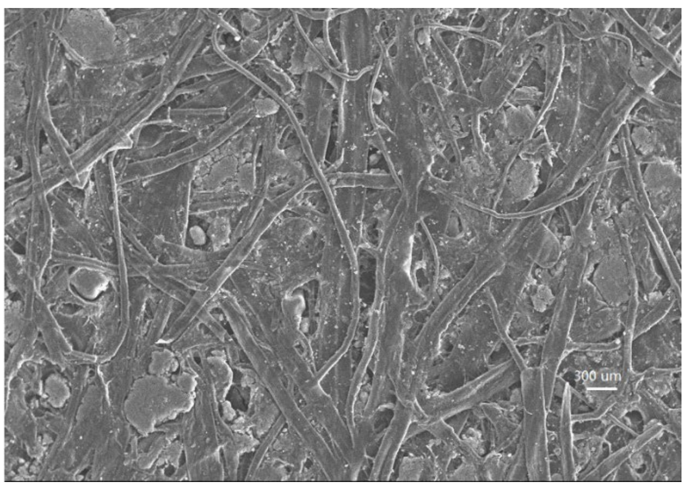

Fig. 5. Experiment III: PFI mixing (30% filler)

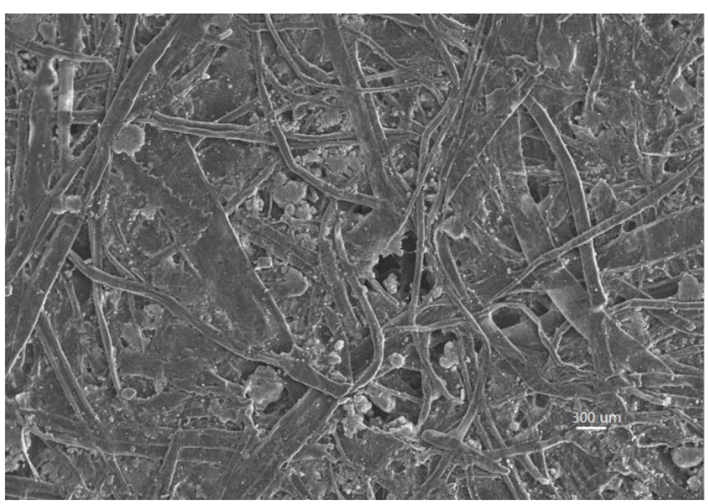

Fig. 6. Experiment III: stirring (30% filler)

Discussion on Test Results

For different fiber raw material ratios (Softwood pulp: hardwood pulp = 10:40 or 20:30, softwood pulp: waste paper pulp 30:35) and different calcium silicate filler addition (30% or 40%), the paper exhibited the advantages of high paper bulk and opacity. Softwood pulp softwood pulp (Tables 2 through 4).

(1) Tables 2 and 3 show that when the filler content was 30%, the fiber raw material with softwood pulp: hardwood pulp = 1:4 had a higher tensile index and burst index than that with softwood pulp: hardwood pulp = 2:3. When the filler content was 40%, the tensile index, tear index, and burst index of the raw material with softwood pulp: hardwood pulp = 2:3 were higher than those of the raw material with a ratio of 1:4. Therefore, when the filler content is less than 30%, the ratio of coniferous wood fiber can have a lower amount of addition, and the paper has a higher strength index, while saving the price of relatively high needle pulp, which can reduce the cost of raw materials. When the filler content was more than 30%, more softwood pulp is needed to improve the strength index of paper.

(2) Different mixing modes of fillers and fibers led to different changes in each property of paper. It can be seen from Tables 2 and 3 that the paper prepared by PFI mixing had high tensile strength and burst strength, and the paper bulk of the paper was low. In the way of mixing and stirring in the fluffer, the paper had high paper bulk and tear strength, while the tensile strength and burst strength of the paper were low. Combined with Figs. 1 through 6, the electron microscopic images of the paper prepared by three groups of experiments with different stirring methods were analyzed, and the photos of each group of experiments were compared and analyzed. The beating process (the beating pressure was 3.33N/mm blade length) makes the calcium silicate particles evenly distributed between the fibers, and increases the bonding point between the filler and the fiber. In this way, compared with the mixed stirring with the fluffer, the smoothness of the paper was better, and the dispersion of the filler was more uniform. The filling amount was also improved without reducing the strength performance index of the paper. Therefore, to ensure the high tensile strength of finished paper, fibers and fillers can be mixed together by disc mill in production to improve the physical strength of finished paper.

(3) The corresponding paper chemicals were selected in the comparison group in the experiment. It can be seen from Tables 2 and 3 that the tensile, tear, burst, and folding strength properties of the finished paper were basically lower than those of the blank sample when the chemicals were successively added into the pulp, but the ash content of the finished paper was increased. This indicated that chemicals increased filler retention, and this caused a reduction of physical strength.

(4) In Experiment III using deinked pulp and calcium silicate (Table 4), after the addition of chemicals, the paper bulk, opacity, tensile strength, and folding resistance of the paper increased, and the filler retention rate increased. Therefore, the use of chemicals not only ensured the improvement of the paper bulk and opacity of the paper, but also increased the tensile strength of the paper, which played a certain role in strengthening. The results showed that the effect of the chemical system selected in the experiment on deinked pulp was better than that of the mixture of coniferous pulp and hardwood pulp.

(5) By comparing the blank paper and the paper with different calcium silicate filler loading ratios, it can be seen that the paper bulk and opacity of the paper were increased significantly with the increase of filler loading ratio. Under the same filling ratio, the ash content, opacity and filler retention of the paper with chemicals were significantly improved compared with the blank paper.

CONCLUSIONS

1. The synthesized calcium silicate can be used as high filling filler for papermaking due to its uniform mixing with fibers in pulp and good adhesion. Paper with chemicals was better than blank paper at the same filling ratio
2. Calcium silicate high-filling paper exhibited the characteristics of higher opacity and high paper bulk, and the paper still had high tensile, tear, and burst strength when the ash content reached 25% to 30%. The addition of chemicals can effectively make the deinked pulp maintain the strength indexes of paper while improving the filler retention.
3. Under the same filling ratio and filling method of calcium silicate filler, the comprehensive performance index of the paper made from softwood pulp and broad-leaf pulp was better than that of the paper made from deinked pulp. The paper obtained higher physical strength by appropriately increasing the proportion of coniferous pulp in the fiber, and the retention of filler could be improved by appropriately increasing the proportion of broad-leaf pulp.
4. After mixing the pulp and calcium silicate filler, and then through the disc grinding and kneading mixing, the calcium silicate filler can be depolymerized and dispersed. At the same time, the pressure of beating makes the depolymerized calcium silicate particles evenly distributed between the fibers, and increases the binding point between the filler and the fiber, so that the obtained paper has higher strength performance than the paper prepared by direct hydrolysis.

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