Effect of the Crystal Shape of Precipitated Calcium Carbonate on the Whiteness of Modified Fly Ash

Huiming Fan, Ping Liu, Xueqin Wang, Da Gao, and Jianan Liu *

Fly ash was modified using calcium oxide and carbon dioxide. The effects of reaction temperature, the rate of carbon dioxide, and the concentration of calcium hydroxide on the crystal shape of precipitated calcium carbonate coated on the surface of fly ash were studied. The effects of the crystal shape of precipitated calcium carbonate on the whiteness of modified fly ash were analyzed. The research showed that the crystal shape of precipitated calcium carbonate was lamellar when the reaction temperature, the rate of carbon dioxide, and the concentration of calcium hydroxide were 20 °C, 0.2 L/min, 20%, respectively, which was conducive to the higher whiteness of modified fly ash.

Keywords: Fly ash; Precipitated Calcium Carbonate; Crystal shape; Whiteness

*Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640, Guangzhou, China; *Corresponding author: 191545996@qq.com*

INTRODUCTION

As the main pollution source of coal-fired power plants, fly ash seriously affects the daily life of residents around coal-fired power plants, and it also has certainly influenced the environment (Gao *et al*. 2003; Li *et al*. 2006; Du 2012; Li *et al*. 2016). At present, fly ash is widely used in agriculture, construction, and other industries. However, the value of such products is low, and the utilization rate is less than 60% (Yang *et al*. 1997; Zhu *et al*. 1999; Huang 2011; Lu *et al*. 2011). Therefore, the use of fly ash in higher value-added industries is valuable. Because the chemical composition and particle morphology of fly ash and kaolinite, which was a kind of papermaking filler, are similar (Sumio *et al*. 2000; Xu and Zhang 2009; He *et al*. 2013; Zhang *et al*. 2013), fly ash can be used as filler in the papermaking industry. However, fly ash is only applicable to the papers with low-whiteness requirements because of its low whiteness (Fu *et al*. 2007).

The main components that affect the whiteness of fly ash is organic carbon and iron compounds (Wang 2015). There are many recent studies on improving the whiteness of the fly ash. Wang (2015) calcined the fly ash and processed the fly ash with acid, and the whiteness of fly ash was increased to 53 ISO.

The energy consumption was too high when calcined at high temperatures, which is impractical for applications in papermaking factories. In addition, the chemical method to remove iron dissolved the main component of fly ash, which damaged its structure. Yang *et al*. (2006) removed carbon in fly ash *via* magnetic separation and flotation separation, and the fly ash was modified with chemical deposition in the $Ca(OH)_2$-H_2O-CO_2 system. This complex process requires a long reaction time and high costs.

Fan *et al*. (2015) modified fly ash in the $Ca(OH)_2$-H_2O-CO_2 system with a single-tube ventilation device. The application of modified fly ash in handsheets was studied. The research was not particularly focused on the crystal morphology of precipitated calcium carbonate coated on the surface of fly ash.

The effects of reaction temperature, the rate of carbon dioxide, and the concentration of calcium hydroxide on the crystal shape of precipitated calcium carbonate on the surface of fly ash were studied in this paper. The effects of the crystal shape of precipitated calcium carbonate on the whiteness of modified fly ash were then analyzed.

EXPERIMENTAL

Materials

Fly ash was supplied from Guangzhou Paper Group Co., Ltd. (Guangzhou, China). Calcium oxide and carbon dioxide were all provided by Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China).

Methods

Screening of fly ash

Different sizes of fly ash particles were obtained from a BSJ-2000 oscillating sieving machine (Yongda Ltd., Xinxiang, Henan, China) using mesh sizes of 200, 250, 300, 325, 400, 500, 600, and 800, the pore size of which were 75 μm, 60 μm, 50 μm, 46.15 μm, 37.5 μm, 30 μm, 25 μm, and 18.75 μm, respectively.

Preparation of modified fly ash

Calcium oxide suspensions of various concentrations were placed in a water bath at 80 °C with stirring at 400 rpm for 1 h. The fly ash of 500 mesh, which accounted for the largest of all mesh sizes and also met the requirements of the particle size of papermaking fillers (fly ash: calcium oxide weight ratio = 1:1), was added to the suspension for 10 min under stirring at 400 rpm. Carbon dioxide was bubbled into the mixture. When the suspension reached pH 7, the experiment was considered complete.

Testing of the whiteness of modified fly ash

The modified fly ash was oven-dried at 105 °C for 2 h (JC202, Congyuan Chemistry Instruments Ltd., Guangzhou, China). After cooling to room temperature, the whiteness of the fly ash was measured using an optical tester (MTCRO-TB-IC, USA) according to ISO 11475 (2004).

Scanning electron microscopy observations of modified fly ash

Dried samples of modified fly ash were mounted on aluminum stubs with tape and sputter-coated with a gold alloy. Samples were observed using an EVO 18 Special Edition scanning electron microscopy (Carl Zeiss, Oberkochen, Germany) operating at an accelerating voltage of 10.0 kV.

RESULTS AND DISCUSSION

The whiteness of the original fly ash was 25.12 ISO. As shown in Table 1, Table 2, and Table 3, the whiteness of modified fly ash was far higher than the original fly ash.

Effects of the Reaction Temperature

As shown in Table 1, the crystal shape of precipitated calcium carbonate was gradually changed with increasing reaction temperature. The crystal shape was changed from lamellar to irregular shape when the reaction temperature was increased from 20 °C to 60 °C. The crystal shape and arrangement of precipitated calcium carbonate were more and more irregular, and the whiteness of the modified fly ash was decreased. The lower reaction temperature was more beneficial for the modified fly ash. The crystal shape of precipitated calcium carbonate was lamellar when the reaction temperature was 20 °C, and the maximum whiteness of the modified fly ash was 59.17 ISO. The crystal shape was irregular when the reaction temperature was 60 °C, and the minimum whiteness of the modified fly ash was 52.79 ISO. The maximum increased by 6.38 ISO compared with the whiteness when the reaction temperature was 60 °C. The whiteness of modified fly ash was greatly increased when the crystal shape of the precipitated calcium carbonate coated on the surface of fly ash was lamellar. The coverage rate, refractive index, and scattering coefficient of the lamellar shape of precipitated calcium carbonate were very good (Yuan and Jin 1998; Wang and Jiang 2004). Compared with the lamellar shape, the whiteness of modified fly ash coated with acicular and irregular shaped crystals of precipitated calcium carbonate was lower. This result was due to the large diameter and poor dispersion of the acicular and irregular shape crystal; thus, the cover effects were poor.

Table 1. Effect of the Reaction Temperature on the Crystal Shape of Precipitated Calcium Carbonate and the Whiteness of Modified Fly Ash

Reaction Temperature (°C)	Whiteness of Modified Fly Ash (ISO)	Crystal Shape of Precipitated Calcium Carbonate
20	59.17	Lamellar
30	57.26	Lamellar and Acicular
40	56.46	Lamellar and Acicular
50	54.33	Acicular
60	52.79	Acicular and Irregular shape

Table 2. Effect of the Rate of Carbon Dioxide on the Crystal Shape of Precipitated Calcium Carbonate and the Whiteness of Modified Fly Ash

Rate of carbon Dioxide (L/min)	Whiteness of Modified Fly Ash (ISO)	Crystal Shape of Precipitated Calcium Carbonate
0.1	59.17	Lamellar
0.2	60.24	Lamellar
0.3	59.07	Lamellar and Globular
0.4	57.75	Globular
0.5	54.32	Globular

Effects of the Rate of Carbon Dioxide

As shown in Table 2, the crystal shape of precipitated calcium carbonate was lamellar when the rate of carbon dioxide was varied from 0.1 L/min to 0.2 L/min, and the whiteness of modified fly ash was gradually improved. The whiteness of the modified fly ash reached a maximum of 60.24 ISO when the rate of carbon dioxide was 0.2 L/min. The crystal shape of precipitated calcium carbonate gradually turned globular when the carbon dioxide flow rate was increased from 0.3 L/min to 0.5 L/min, and the whiteness of the modified fly ash was decreased. The whiteness of the modified fly ash reached a minimum of 54.32 ISO when the flow of carbon dioxide was 0.5 L/min. The maximum increased by

5.92 ISO compared with the whiteness when the rate of carbon dioxide was 0.5 L/min. This result indicates that the globular crystal was concentrated and could not be formed into a thin and uniform coating in the modified process. Also, the aggregation phenomenon might have occurred between the precipitated calcium carbonate, which all greatly affected the coating effects of modification. The lamellar crystal had the advantages of regular shape and large specific surface area, which all contributed to the great modified effects.

Effects of the Concentration of Calcium Hydroxide

Table 3 shows that the crystal shape of precipitated calcium carbonate gradually changed from irregular to acicular and lamellar when the concentration of calcium hydroxide was increased from 5% to 20%, and the whiteness was also gradually increased. The dispersibility of the irregular shape of the crystal was poor, which could not be effectively coated on the surface of fly ash. Compared with the irregular shape, the acicular crystals tended to interweave, which contributed to the relatively good cover effects. The crystal shape of precipitated calcium carbonate was globular when the concentration of calcium hydroxide increased from 20% to 25%, and the whiteness of the modified fly ash was decreased. This result might be due to the aggregation appearing in the modified process, which caused most of the fly ash to remain uncoated.

Table 3. Effect of the Concentration of Calcium Hydroxide on the Crystal Shape of Precipitated Calcium Carbonate and the Whiteness of Modified Fly Ash

Concentration of Calcium Hydroxide (%)	Whiteness of Modified Fly Ash (ISO)	Crystal Shape of Precipitated Calcium Carbonate
5	57.36	Irregular shape
10	59.17	Irregular shape
15	60.28	Acicular and Irregular shape
20	62.33	Lamellar
25	59.85	Lamellar and Globular

SEM Observations of Modified Fly Ash

Figures 1 through 4 showed SEM images of the morphology of original fly ash and the crystal shapes of the precipitated calcium carbonate coating on the surface of fly ash.

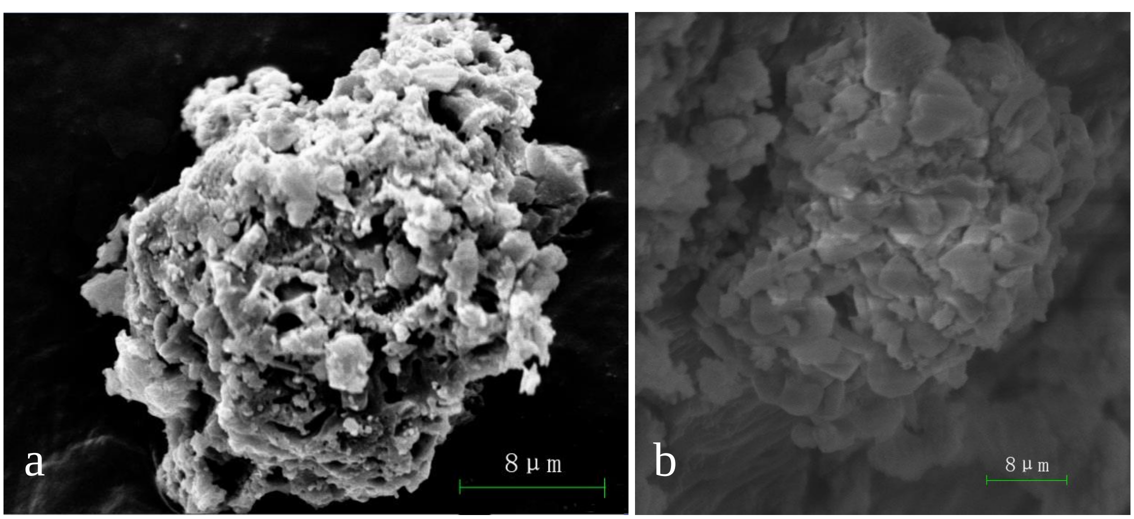

Fig. 1. SEM images of original fly ash (a) and modified fly ash coated with lamellar (b) crystal of precipitated calcium carbonate

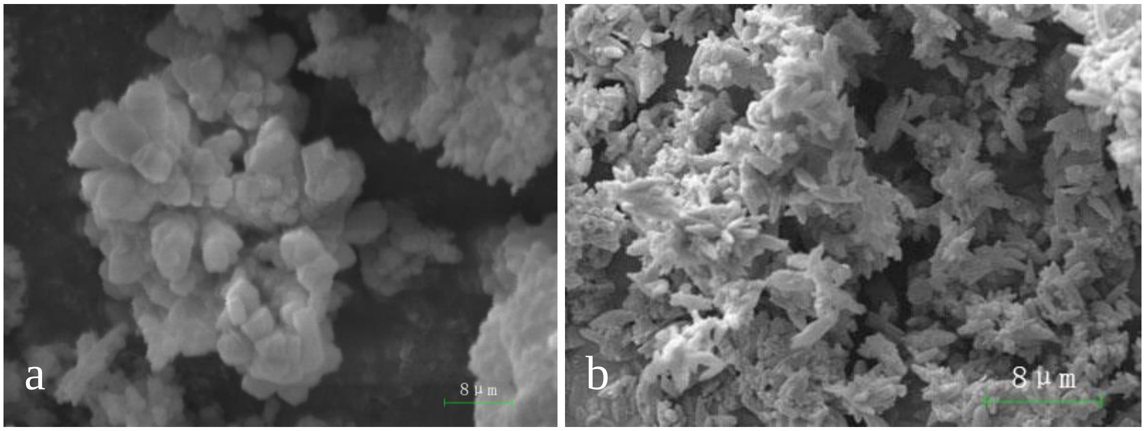

Fig. 2. SEM images of modified fly ash coated with globular (a) and acicular (b) crystal of precipitated calcium carbonate

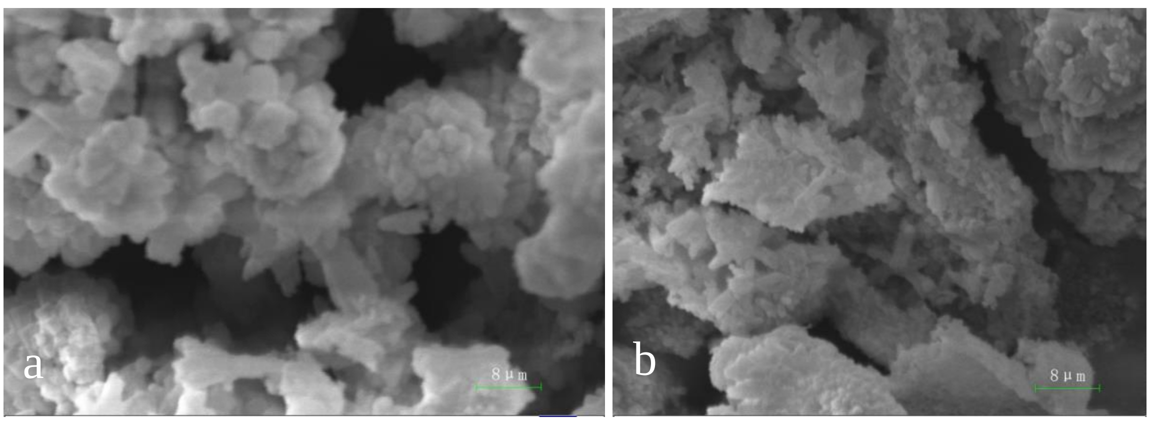

Fig. 3. SEM images of modified fly ash coated with irregular shape (a) and acicular & irregular shape crystal (b) crystal of precipitated calcium carbonate

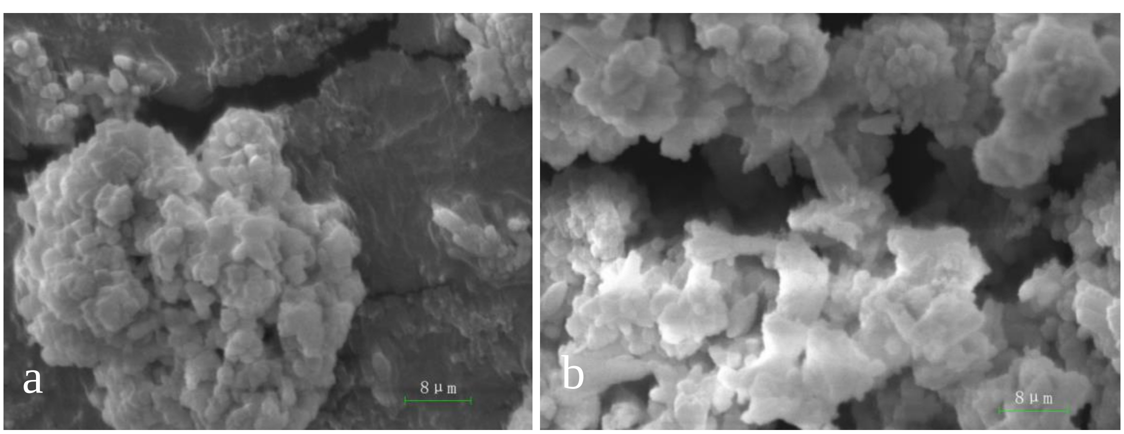

Fig. 4. SEM images of modified fly ash coated with lamellar & globular (a) and lamellar & acicular (b) crystal of precipitated calcium carbonate

Compared with the modified fly ash, the surface morphology of original fly ash was porous. Compared with the other crystal shape, the fly ash was coated with lamellar crystal tightly. For the other crystal shapes, such as acicular, globular, and irregular shape, there was obvious aggregation, which greatly influenced the whiteness of modified fly ash.

CONCLUSIONS

1. The crystal shape of precipitated calcium carbonate was changed from lamellar to acicular and irregular shape with increasing reaction temperature, and the whiteness of the modified fly ash was decreased. The crystal shape of precipitated calcium carbonate was lamellar when the reaction temperature was 20 °C, and the whiteness of modified fly ash reached 59.17 ISO.
2. The crystal shape of precipitated calcium carbonate was changed from lamellar to globular when the flow rate of carbon dioxide was increased. The crystal shape of precipitated calcium carbonate was lamellar when the rate of carbon dioxide was 0.2 L/min, and the whiteness of modified fly ash reached 60.24 ISO.
3. The crystal shape of precipitated calcium carbonate was changed from irregular shape to acicular, lamellar, and globular when the concentration of calcium hydroxide was increased. The crystal shape of precipitated calcium carbonate was lamellar when the concentration of calcium hydroxide was 20%, and the whiteness of modified fly ash reached 62.33 ISO.
4. Compared with irregular shape, acicular, and globular, the whiteness of modified fly ash was greatly improved as the crystal shape of precipitated calcium carbonate coated on the surface of fly ash was lamellar because of its large coverage rate, high refractive index, and large scattering coefficient.

ACKNOWLEDGMENTS

This work was supported by the Fundamental Research Funds (No. 2016C04) for the State Key Lab of Pulp ＆ Paper Engineering and the Science and Technology Plan Projects of Guangdong Province (No. 2016A020221040).

REFERENCES CITED

Du, S. Y. (2012). “Research on high fly ash content and light weight insulating blocks,” *Fly Ash Comprehensive Utilization* (5), 45-48. DOI: 10.3969/j.issn.1005-8249.2012.05.015

Fan, H. M., Wang, S., Liu, J. A., and Long, J. (2015). “Improving fly ash whiteness and the influence of modified fly ash on the physical strength of paper,” *BioResources* 10(4), 7434-7441. DOI: 10.15376/biores.10.4.7434-7441

Fu, J. S., Zhang, J. L., Li, Y., and Huang, Z. X. (2007). “Study of application of fly-ash in corrugated paper,” *Journal of Hubei University of Technology* 22(6), 6-20. DOI: 10.3969/j.issn.1003-4684.2007.06.002

Gao, Z. G., Hua, L., Zhen, H. J., and Zhang, Z. G. (2003). "Physical and chemical properties of fly ash and its resource utilization," *Journal of Capital Normal University* 24(1), 72-76. DOI: 10.3969/j.issn.1004-9398.2003.01.018

He, L., Zhao, L. H., and He, B. H. (2013). "White mud pretreatment with PEI and the study of its influence on AKD sizing as filler," *Paper Science & Technology* 32(4), 58-63.

Huang, Q. (2011). "Analysis of development prospects and status quo of comprehensive utilization of fly ash at home and abroad," *China Well and Rock Salt* 7(4), 41-43. DOI: 10.3969/j.issn.1001-0335.2011.04.015

ISO 11475 (2004). "Paper and board -- Determination of CIE whiteness, D65/10 degrees (outdoor daylight)," International Organization for Standardization, Geneva, Switzerland.

Li, H., Shang, B. M., Feng, S. H., Wu, H. X., and Lan, J. S. (2006). "Research on physical and chemical properties and microstructure of fly ash grain," *Coal Ash China* (6), 18-20. DOI: 10.3969/j.issn.1007-046X.2006.05.006

Li, M., Zhang, Y. J., and Jin, H. X. (2016). "The present situation and prospect of comprehensive utilization of fly ash in China," *Value Engineering* 16(3), 183-185.

Lu, G. Y., Xue, F., and Zhao, J. T. (2011). "Some advice to the fly ash of China," *China Mining Magazine* 20, 194-200.

Sumio, H., Masato, K., and Kazuya, Y. (2000). "Effective use of fly ash slurry as fill material," *Journal of Hazardous Materials* (76), 301-337.

Wang, G. Q., and Jiang, X. C. (2004). "Application of superfine lamellar precipitated calcium carbonate in paper coating," *Paper Chemicals* 16(6), 41-43. DOI: 10.3969/j.issn.1007-2225.2004.06.010

Wang, M. (2015). *The Study of Whitening Coal Fly-Ash*, M.S. thesis, South China University of Technology, Guangzhou, China.

Xu, Y., and Zhang, J. Y. (2009). "Effects of pulverized coal fly-ash addition as a wet-end filler in papermaking," *World Pulp and Paper* 28(1), 6-13.

Yang, J. H., Che, F. C., Wang, D. Y., Xie, D. T., Wei, C. F., and Zhang, L. (1997). "Study of physical and chemical properties and agricultural chemical behavior of fly ash," *Journal of Plant Nutrition and Fertilizer* 3(4), 341-348. DOI: 10.11674/zwyf.1997.0409

Yang, Y. F., Gai, G. S., and Cai, Z. F. (2006). "Surface modification of purified fly ash and its application in polymer," *Journal of Hazardous Materials* 133(1), 276-282. DOI: 10.1016/j.jhazmat.2005.10.028

Yuan, W., and Jin, X. (1998). "Preparation of the lamellar precipitated calcium carbonate for paper coating," *Fine Chemicals* 15(2), 26-29.

Zhang, M., Song, S., and Wang, J. (2013). "Using a novel fly ash based calcium silicate as a potential paper filler," *BioResources* 8(2), 2768-2779. DOI: 10.15376/biores.8.2.2768-2779

Zhu, J., Zhou, J., Cao, D. J., and Jia, M. X. (1999). "Physical and chemical properties of fly ash and its application in agriculture," *Anhui Agriculture Science* 5(1), 48-49.

Article submitted: October 17, 2016; Peer review completed: November 20, 2016; Revised version received and accepted: November 21, 2016; Published: November 30, 2016.
DOI: 10.15376/biores.12.1.655-661