Effect of the Formulation Control Agent on Brightness of Modified Fly Ash and Its Potential Application in Papermaking

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Different agents were used to control the crystalline morphology of calcium carbonate on the surface of fly ash, which was then used as a papermaking filler in an attempt to improve the utilization rate of fly ash and reduce the dust pollution problem. A mixed solution of calcium hydroxide and fly ash was used as the raw materials, and then three crystal form control agents were tested: $(NaPO_3)_6$, $ZnCl_2$, and $Na_2B_4O_7 \cdot 10H_2O$. A certain amount of carbon dioxide was bubbled into the mixture to form a precipitated calcium carbonate deposit on the surface of fly ash. The calcium carbonate on the fly ash surface was altered by changing the amount of crystal form control agent to determine the best coating effect. The results showed that at the 0.35% $ZnCl_2$ dosage (relative to the theoretical quantity of the calcium carbonate), the surface of the fly ash was uniformly coated with a layer of spherical calcium carbonate crystals and there was a good coating effect. The highest fly ash brightness obtained was 65.3% ISO, and when this fly ash was used as a paper filler, the paper brightness was 75.6% ISO. More importantly, this study demonstrated the potential of fly ash in papermaking.

Keywords: Coating modification; Fly ash; Precipitated calcium carbonate; Crystal form control agent; Brightness

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INTRODUCTION

Fly ash is an industrial byproduct that is mainly produced by combustion in thermal power plants and urban solid waste incineration. To an extent, fly ash poses a serious threat to the global climate, aviation flight, and human health (Hansen *et al*. 1997; Ramanathan *et al*. 2001; Sear 2001; Pöschl 2005; Dong *et al*. 2015). Therefore, there is an urgent need to treat fly ash. If it is not handled properly, it is a waste of a renewable resource. Although the utilization of fly ash has been achieved in some aspects (Gao *et al*. 2003), its utilization rate is still low, and as such potential applications of fly ash have not yet been determined (Aydin and Balkis 2017). The interest in fly ash has sharply increased lately because of the specific chemical and physical properties of the material. Fly ash has huge potential for application in the paper industry because of its size, shape, and chemical composition, which are similar to that of the paper-making filler kaolin (Horiuchi 2000; Zhang *et al*. 2013).

However, the use of fly ash in filler applications is still rare because of its low brightness values of only 30% to 40% and low friction of its untreated surface. Therefore, the brightness of fly ash needs to be increased with a suitable method to broaden its application as a filler. After the Japanese scholar Okubo proposed the new concept of "particle design" in the 1980s, the research and development of composite particles with a core-shell structure have been favored, and a large number of composite powders with core-shell structures have been developed (Okubo *et al*. 1980; Okubo *et al*. 1981; Okubo *et al*. 1982; Fan 2004). In recent years, powder surface coating modification technology has developed rapidly and is widely used (Fan *et al*. 2012, 2014, 2015). Yang *et al*. (2006) modified the surface of microbeads in fly ash with a $Ca(OH)_2$-H_2O-CO_2 system to increase the surface brightness and roughness. However, because of the different structures of fly ash produced by different factories, the shape of calcium carbonate crystals modified by coating is irregular. Thus, the application of fly ash with a coating modification by this method has not been widely used.

This paper discusses the effect of coating in the process of fly ash coating modification and its future related problems in applications as a paper filler. Fly ash and paper filler have similar physical structures and chemical properties. However, to date, no one has used a different crystal form control agent to control the formation of calcium carbonate crystals on fly ash. In 2015, coal-fired power plants in China emitted 550 million tons of emissions, which increased to 565 million tons in 2016 (SEPA 2015, 2016). Therefore, research on improving the utilization rate of fly ash is of practical significance.

EXPERIMENTAL

Materials

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

Methods

Analytical method

The surface morphology of the fly ash before and after the coating modification was observed with an EVO 18 scanning electron microscope (SEM) (OPTON, Oberkochen, Germany). The paper was kept in a constant temperature and humidity chamber (23 °C ± 1 °C; 50% ± 2% RH) to balance the 24-h moisture content. A L & W brightness meter (Kista, Sweden) was used on the modified fly ash particles and modified fly ash plus paper to test the brightness. Bleached hardwood pulp with a beating degree of 32° SR (without any filler and an auxiliary whiteboard of 79.9% ISO) was provided by Guangzhou Paper Group Co., Ltd. (Guangzhou, China).

Fly ash coating modification

First, a certain amount of calcium oxide was digested at 85 °C for 1 h. After digestion was completed and the material was cooled, the bottom residue was filtered to obtain a calcium hydroxide suspension and the solid content was measured. Calcium oxide and the 500-mesh fly ash was mixed at a weight ratio of 1:1. After the 7% concentration of calcium hydroxide suspension and fly ash were mixed, a certain amount of $(NaPO_3)_6$, $ZnCl_2$, or $Na_2B_4O_7{\cdot}10H_2O$ were added before the start of the reaction as the crystal-type controlling agent (relative to the theoretically produced calcium carbonate quantity), which is shown in Table 1. The mixture was stirred at 500 rpm with uniform mixing for about 10 min. Pure carbon dioxide gas was introduced at a rate of 0.15 L/min. When the reaction started, the pH value of the reaction solution was monitored in real-time with a pH meter.

The reaction was immediately terminated when the pH became 7 to obtain the modified fly ash.

Table 1. Different Crystal Control Agents Used

Crystal Control Agent	Amount Added (wt.%)					
$(NaPO_3)_6$	0.00	0.10	0.15	0.20	0.25	0.30
$ZnCl_2$	0.00	0.20	0.30	0.30	0.35	0.40
$Na_2B_4O_7 \cdot 10H_2O$	0.00	0.25	0.30	0.35	0.40	0.45

Modified fly ash and papermaking

First, 0.36 g of modified fly ash particles were weighed, added to 1.08 g of slurry, and then dispersed with agitation at 5000 rpm. Then 0.05% of cationic polyacrylamide (relative to the absolute dry pulp) was added as a retention aid, and the mixture was stirred with a glass rod. After papermaking on a laboratory sheet former, the wet paper sheet was placed on the drying section of the sheet former for drying.(drying pressure = 0.08 MPa, temperature = 90 °C, and time = 10 min). Finally, the brightness of the paper was measured. The amount of paper filling was 25%, which was 72 g/m^2.

RESULTS AND DISCUSSION

Effects of $(NaPO_3)_6$ as the Crystal Form Control Agent

To obtain better calcium carbonate-coated fly ash, the optimum amount of crystal control agent must be determined. Figure 1 shows the SEM micrographs of the surface morphologies of the coated fly ash with different amounts of $(NaPO_3)_6$. In the absence of any form of control agent, which is shown in Fig. 1a, the calcium carbonate basically formed random or spindle-like morphologies. Figure 1 shows that the $(NaPO_3)_6$ tended to pinch the calcium carbonate onto the fly ash surface because the crystal form control agent was added prior to the start of the reaction. This control agent will adsorb onto the initial formation of the calcium carbonate nucleus surface, which greatly reduces the energy barrier for the nucleation. Because the crystal-type controlling agent was adsorbed onto the specific surface of the calcium carbonate nucleus, the growth activity of the calcium carbonate crystal in a specific direction was large and the growth in other directions was suppressed, which resulted in a one-way growth trend.

Table 2. Effect of $(NaPO_3)_6$ as the Crystalline Formulation Control Agent on the Brightness of the Modified Fly Ash

$(NaPO_3)_6$ Dosage (%)	Modified Fly Ash Brightness (ISO)	Modified Fly Ash Plus Paper Brightness (ISO)
0.00	62.27	72.64
0.10	62.33	72.77
0.15	62.79	73.45
0.20	64.01	74.66
0.25	64.67	74.89
0.30	61.34	72.01

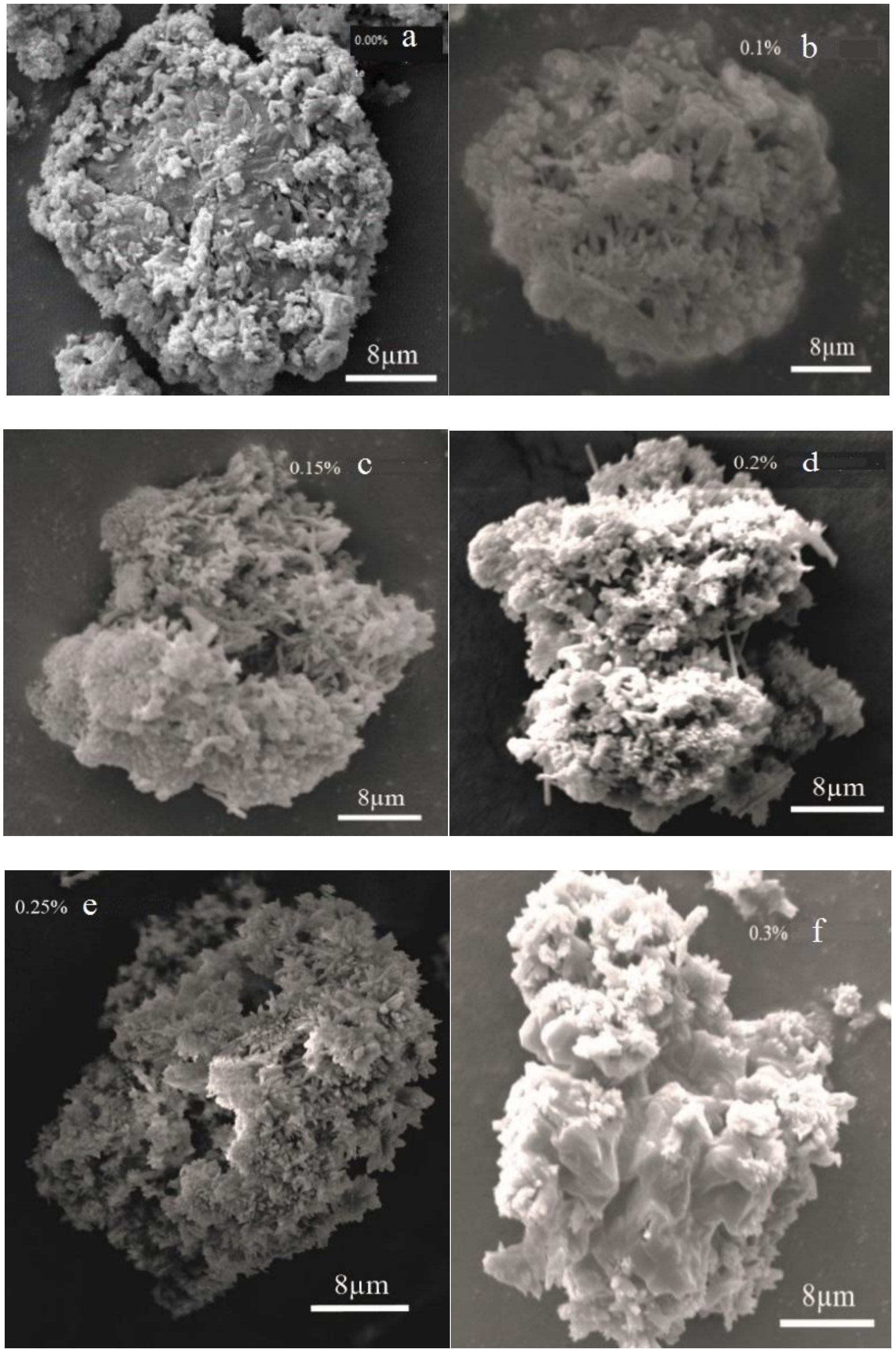

Fig. 1. SEM images of the modified fly ash with different amounts of $(NaPO_3)_6$: a) 0%; b) 0.1%; c) 0.15%; d) 0.2%; e) 0.25%; and f) 0.3%

Table 2 and Figs. 1b, 1c, 1d, and 1e show that as the amount of $(NaPO_3)_6$ increased, the calcium carbonate crystals on the surface of the fly ash gradually became needle-shaped. The modified fly ash brightness gradually increased. When the amount of $(NaPO_3)_6$ was 0.25%, as is shown in Fig. 1e, the surface of the fly ash was coated with a uniform layer of needle-shaped calcium carbonate crystals. The brightness of the fly ash reached a maximum of 64.7% ISO and the brightness of the filler paper was 74.9% ISO. When the amount of $(NaPO_3)_6$ increased to 0.3% (Fig. 1f), the fly ash surface was coated with large and irregularly-shaped calcium carbonate crystals. At this point, the brightness of the modified fly ash began to decrease. This may have been because when the amount of $(NaPO_3)_6$ was out of the proper range, the selectivity of the $(NaPO_3)_6$ to the crystal nucleus of the calcium carbonate deteriorated and a massive coating modification occurred with poor coverage. In addition, it may be because of the existence of Na^+. The ionization balance of $Ca(OH)_2=Ca^{2+} +2OH^-$ is destroyed, which affects the nucleation process of calcium carbonate crystals on fly ash surface.

Effects of $ZnCl_2$ as the Crystal Form Control Agent

Table 3 shows that when the dosage of $ZnCl_2$ was 0.20%, the modified fly ash and filler paper brightness were reduced. Figure 2a shows that when 0.20% $ZnCl_2$ was added, the modified fly ash particles were coated with a large number of irregular calcium carbonate aggregates. A phenomenon where the calcium carbonate agglomerated into blocks was observed, which was because a small amount of $ZnCl_2$ crystal form control agent was not able to effectively control the crystal morphology of calcium carbonate on the surface of the fly ash. Some of the calcium carbonate nuclei were chlorinated by the $ZnCl_2$. The formation of small-sized and irregular calcium carbonate crystal particles on the fly ash surface may be unstable, the interface can be higher, and the subsequent precipitation of calcium carbonate crystals easily combined to reduce the concentration. The surface resulted in the crystallization system achieving a relatively stable state, and as such large aggregates coated on the fly ash surface appeared. These large pieces of calcium carbonate aggregates can easily fall off under outside action, which resulted in a modified fly ash with a reduced degree of brightness.

The morphologies of the modified fly ash with $ZnCl_2$ concentrations of 0.25% and 0.30% are shown in Figs. 2b and 2c, respectively. Figure 2b shows that when the amount of $ZnCl_2$ was 0.25%, some of the calcium carbonate crystals were spherical, but most of the crystals were short and rod-shaped. When the amount of $ZnCl_2$ increased from 0.25% to 0.30%, the amount of spherical calcium carbonate crystal particles increased. As the $ZnCl_2$ dosage increased, the shape of the calcium carbonate crystals on the surface of the modified fly ash gradually changed from irregular to quasi-spherical. Table 3 shows that when a large amount of $ZnCl_2$ was added, a large part of the calcium carbonate crystal nucleus was formed under the action of $ZnCl_2$ to form spherical crystals, and the particle size was relatively uniform. The number of large bulky calcium carbonate crystals formed was also decreasing. The surface covering performance and the brightness were improved when the spherical crystals were crystallized on the surface of the fly ash compared with the random crystal morphology. The non-uniform nucleation on the surface of the fly ash was more uniform and the covering property was better. When the dosage of $ZnCl_2$ was 0.35%, the brightness of the modified fly ash reached its maximum at 65.3% ISO, which was an increase of 3.1% ISO compared with the modified fly ash without $ZnCl_2$. Figure 2d shows the modified fly ash surface was uniformly coated with a layer of spherical calcium carbonate crystals, which improved the modified pulverized coal gray brightness and surface coating effect to a certain extent. As the amount of $ZnCl_2$ increased to 0.4%, the brightness of the modified fly ash began to decrease, and it was not remarkably different from the brightness of the modified fly ash without $ZnCl_2$. This may have been because an excessive amount of $ZnCl_2$ produces too much amphoteric zinc hydroxide, and so the control agent was not able to control the shape of the crystals. When the calcium carbonate crystals crystallized on the fly ash surface, zinc hydroxide may have been adsorbed on the crystal surface with the adjacent part of the calcium carbonate crystals causing electrostatic repulsion, which caused the crystal layer to have a loose state and resulted in exposed fly ash.

Table 3. Effect of $ZnCl_2$ as the Crystalline Control Agent on the Brightness of the Modified Fly Ash

$ZnCl_2$ Dosage (%)	Modified Fly Ash Brightness (ISO)	Modified Fly Ash Plus Paper Brightness (ISO)
0.00	62.27	72.64
0.20	61.85	72.07
0.25	62.91	73.69
0.30	64.12	74.22
0.35	65.33	75.59
0.40	62.41	72.69

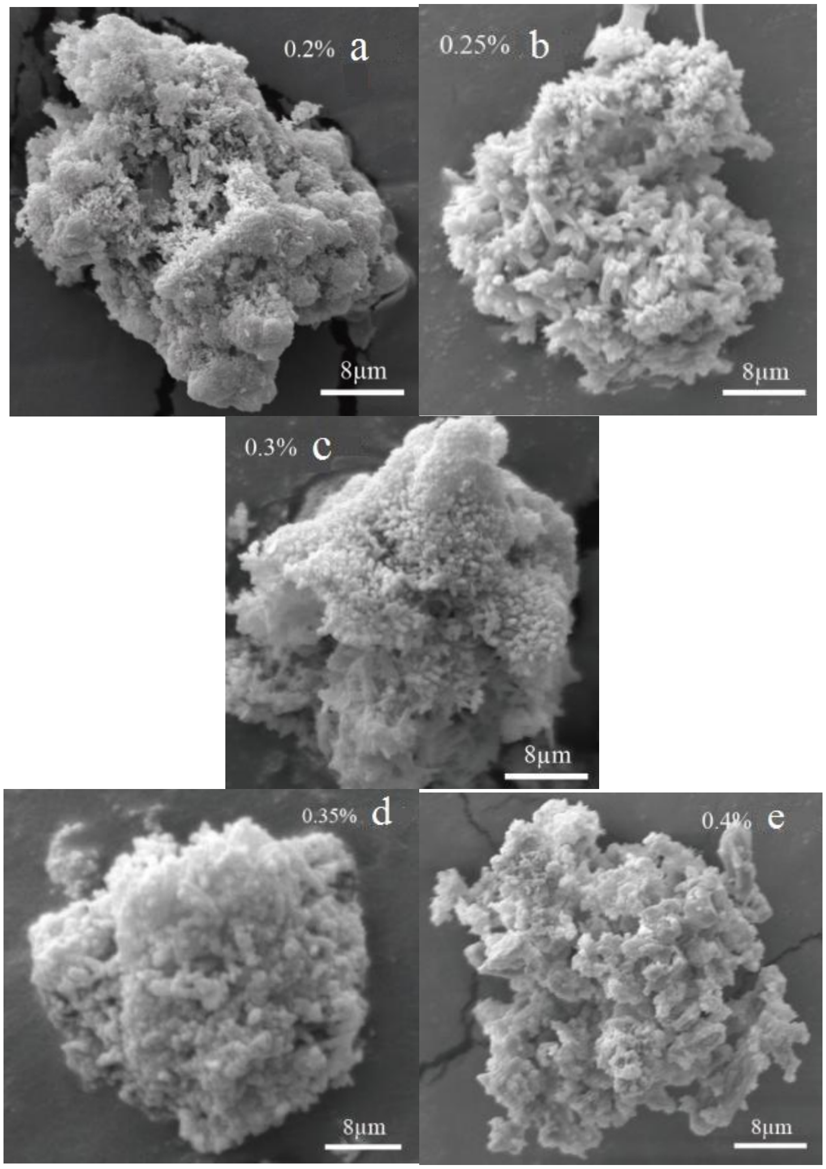

Fig. 2. SEM images of the modified fly ash with different amounts of $ZnCl_2$: a) 0.2%; b) 0.25%; c) 0.3%; d) 0.35%; and e) 0.4%

Effects of $Na_2B_4O_7 \cdot 10H_2O$ as the Crystallization Control Agent

Table 4 shows that when the amounts of $Na_2B_4O_7 \cdot 10H_2O$ added were 0.25% and 0.30%, the modified fly ash and filler paper had only slightly increased brightness values. Figures 3a and 3b show that the surfaces of the modified fly ash were coated with crystals similar to flaky calcium carbonate particles, and there were some irregular-shaped crystal particles. From these two figures, we could see that the particle size of calcium carbonate particles formed on the surface of fly ash is larger. This may have been because when the control agent was not added, the crystal form had a less than good crystal morphology and particle size control. In contrast, the existence of flaky crystal particles in the horizontal growth mode on the fly ash surface and the crystal layer coating shape were conducive to improving the surface of the fly ash, and so the modified fly ash filler had a slight increase in the brightness when the amount of $Na_2B_4O_7 \cdot 10H_2O$ added was 0.35%. Figure 3c shows that the modified fly ash surface had flaky carbonic acid particles. The particle size of the calcium crystal particles was smaller than when 0.25% and 0.30% $Na_2B_4O_7{\cdot}10H_2O$ were added, but it was observed that there were still some large flaky crystal particles. These crystal particles were not needle-like or spherical like when $(NaPO_3)_6$ and $ZnCl_2$ were added, but had an ordered crystal arrangement. When the amount of $Na_2B_4O_7{\cdot}10H_2O$ added was 0.40%, the maximum brightness of the modified fly ash was 63.8% ISO. Figure 3d shows that the modified fly ash surface was crystallized. In contrast with the above case, the flake-like crystal particles of one layer with different grain sizes were crystallized on the surface of the fly ash in a longitudinally extending manner. This may have been because of the fact that the crystal form of the control agent achieved a better saturation. Compared with the horizontal lamellae, the leaf-like structure formed by the longitudinal stretching process was explained by the oriented attachment crystallization mechanism proposed by Penn and Banfield (2003), which refers to a certain crystal structure. In the process of growth, the grains do not use atoms or molecules as growth units, but rather follow the principle of crystal face matching. Small micro- and nano-particles are the growth units and are oriented in a crystallographically consistent direction. Finally, the process of growing crystals occurred; that is, the calcium carbonate crystal crystallized on the surface of the fly ash in a form of bottom-up nano-particle assembly and regrowth. The nano-particles share a crystal plane, which can greatly reduce the surface energy and make the system more stable. This kind of crystal growth pattern can greatly improve the covering effect of the fly ash surface through jungle interweaving, and the stability is also good (Penn and Banfield 2003). When the amount of $Na_2B_4O_7{\cdot}10H_2O$ increased to 0.45%, it was observed in Fig. 3e that the crystalline calcium carbonate particles on the fly ash surface were chaotic and disordered, but there was also a small amount of massive crystals. This may have been caused by the high content of $Na_2B_4O_7{\cdot}10H_2O$ in the solution. When the concentration is high, $Na_2B_4O_7{\cdot}10H_2O$ not only regulates the crystal morphology, but can also affect the state of the entire reaction system. This caused the aggregation of micro- and nano-crystal particles, which affected the non-uniform nucleation process of calcium carbonate crystals on the surface of the fly ash.

Table 4. Effect of $Na_2B_4O_7{\cdot}10H_2O$ as the Crystalline Control Agent on the Brightness of the Modified Fly Ash

$Na_2B_4O_7{\cdot}10H_2O$ Dosage (%)	Modified Fly Ash Brightness (ISO)	Modified Fly Ash Plus Paper Brightness (ISO)
0.00	62.27	72.64
0.25	62.51	72.70
0.30	62.86	72.88
0.35	63.00	73.09
0.40	63.85	73.56
0.45	62.22	73.33

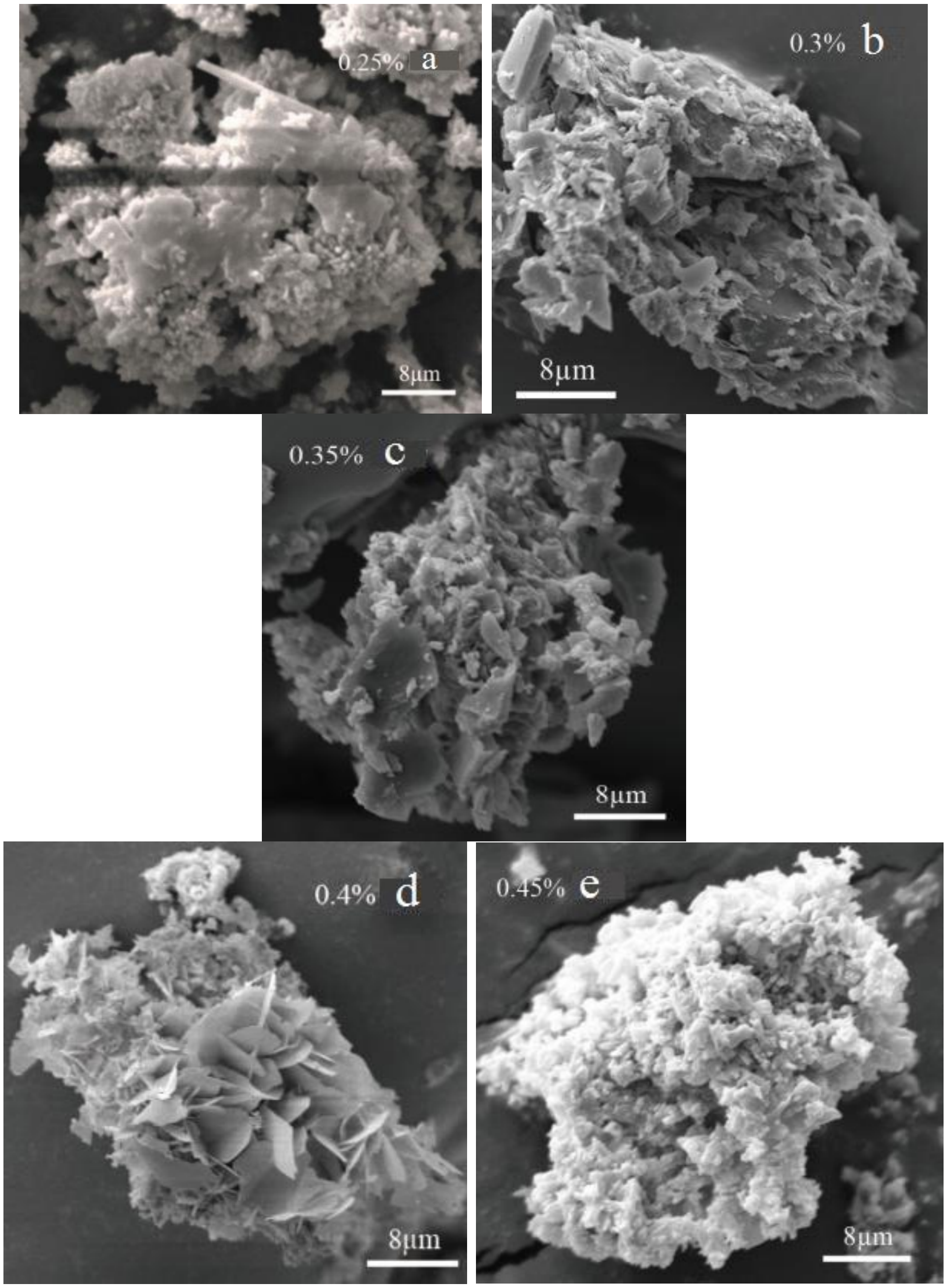

Fig. 3. SEM images of the modified fly ash with different amounts of $Na_2B_4O_7\cdot 10H_2O$: a) 0.25%; b) 0.3%; c) 0.35%; d) 0.4%; and e) 0.45%

CONCLUSIONS

1. The crystal form control agents have a significant positive impact on the brightness value and appearance of the fly ash coated. Compared with no addition of the crystal control agent, the brightness of the fly ash modified is greatly increased. Addition of the crystal control agents achieves a better coating effect of the fly ash by adsorbing onto the initial formation of the calcium carbonate nucleus surface, which greatly reduces the energy barrier of the nucleus and producing a uniform layer of calcium

carbonate crystals on the surface of the fly ash.

2. The high amount of added the crystal control agents exhibits an inverse effect on the brightness value and appearance of the fly ash coated. They improved by increasing the crystal control agents content by up to 0.25% for $(NaPO_3)_6$, 0.35% for $ZnCl_2$ and 0.25% for $Na_2B_4O_7 \cdot 10H_2O$ additive by weight, decreasing thereafter. When the amount of the crystal control agents was out of the proper range, the selectivity of the crystal nucleus of the calcium carbonate deteriorated and a massive coating modification occurred with poor coverage.
3. The addition of 0.35% $ZnCl_2$ resulted in the optimum coating effect on the surface of the fly ash, most likely because the addition of $(NaPO_3)_6$ caused needle-shaped calcium carbonate crystals to form on the surface of the fly ash, which were intertwined and may have had gaps. The crystal morphology of the flaky calcium carbonate crystals obtained by adding $Na_2B_4O_7 \cdot 10H_2O$ was not uniform and showed a disorderly coating state on the surface of the fly ash.
4. Only from the aspect of improving the brightness of paper, the addition of 0.35% $ZnCl_2$ were found to be the optimum proportions for its application in papermaking.

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REFERENCES CITED

Aydin, E., and Balkis, A. P. (2017). "Preliminary study on the durability properties of high-volume fly ash mortar composites," *J. Test. Eval.* 45(6), 2029-2038. DOI: 10.1520/JTE20160221

Dong, J., Zhao, J. M., and Liu, L. H. (2015). "Morphological effects on the radiative properties of soot aerosols in different internally mixing states with sulfate," *J. Quant. Spectrosc. Ra.* 165, 43-55. DOI: 10.1016/j.jqsrt.2015.06.025

Fan, S. (2004). *Surface Modification of Mineral Powder Nano-technology Research and Application*, Ph.D. Dissertation, Tsinghua University, Beijing, China.

Fan, H., Wang, D., Bai, W., and Liu, J. (2012). "Starch-sodium stearate complex modified PCC filler and its application in papermaking," *BioResources* 7(3), 3317-3326. DOI: 10.15376/biores.7.3.3317-3326

Fan, H., Wang, X., Liu, J., and Xu, B. (2015). "Study of coating weight and utilization rate in the modification of ground calcium carbonate," *BioResources* 10(4), 6861-6871. DOI: 10.15376/biores.10.4.6861-6871

Fan, H., Xu, B., Liu, J., and Zhang, C. (2014). "Effect of starch dosage on the properties of modified ground calcium carbonate," *BioResources* 9(3), 4679-4689. DOI: 10.15376/biores.9.3.4679-4689

Gao, Z., Hua, L., Zheng, H., and Zhang, Z. (2003). "Physicochemical characteristics of fly ashes and situation & prospect of its utilization as resources," *Journal of Capital*

Normal University (Natural Sciences) 24(1), 70-77.

Hansen, J., Sato, M., and Ruedy, R. (1997). "Radiative forcing and climate response," *J. Geophys. Res.* 102, 6831-6864. DOI: 10.1029/96JD03436

Horiuchi, S., Kawaguchi, M., and Yasuhara, K. (2000). "Effective use of fly ash slurry as fill material," *J. Hazard. Mater.* 76(2–3), 301-337. DOI: 10.1016/S0304-3894(00)00205-3

Okubo, M., Ando, M., Yamada, A., Katsuta, Y., and Matsumoto, T. (1981). "Studies on suspension and emulsion. XLVII. Anomalous composite polymer emulsion particles with voids produced by seeded emulsion polymerization," *J. Polym. Sci. Polym. Lett.* 19(3), 143-147. DOI: 10.1002/pol.1981.130190310

Okubo, M., Katsuta, Y., and Matsumoto, T. (1982). "Studies on suspension and emulsion. LI. Peculiar morphology of composite polymer particles produced by seeded emulsion polymerization," *J. Polym. Sci. Polym. Lett.* 20(1), 45–51. DOI: 10.1002/pol.1982.130200107

Okubo, M., Yamada, A., and Matsumoto, T. (1980). "Estimation of morphology of composite polymer emulsion particles by the soap titration method," *J. Polym. Sci. Pol. Chem.* 18(11), 3219-3228. DOI: 10.1002/pol.1980.170181108

Penn, R. L., and Banfield, J. F. (1998). "Imperfect oriented attachment: Dislocation generation in defect-free nanocrystals," *Science* 281(5379), 969-971. DOI: 10.1126/science.281.5379.969

Pöschl, U. (2005). "Atmospheric aerosols: Composition, transformation, climate and health effects," *Angew. Chem. Int. Edit.* 44(46), 7520-7540. DOI: 10.1002/anie.200501122

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D. (2001). "Aerosols, climate, and the hydrological cycle," *Science* 294(5549), 2119-2124. DOI: 10.1126/science.1064034

Sear, L. K. A. (2001). "Fly ash and the environment," in: *Properties and Use of Coal Fly Ash: A Valuable Industrial By-product*, Thomas Telford Ltd., London, UK, pp. 30-62.

SEPA (2015). *Report on the State of the Environment 2015*, State Environmental Protection Administration of China (SEPA), Beijing, China.

SEPA (2016). *Report on the State of the Environment 2016*, State Environmental Protection Administration of China (SEPA), Beijing, China.

Yang, Y.-F., Gai, G.-S., Cai, Z.-F., and Chen, Q.-R. (2006). "Surface modification of purified fly ash and application in polymer," *J. Hazard. Mater.* 133(1-3), 276-286. DOI: 10.1016/j.jhazmat.2005.10.028

Zhang, M., Song, S., Wang, J., Sun, J., Li, J. Z., Ni, Y., and Wei, X. (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

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