Effect of Crystal-shaped Additives of Precipitated Calcium Carbonate on the Whiteness of Modified Fly Ash and Hand Sheets

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Fly ash was modified using calcium oxide and carbon dioxide. The morphology of precipitated calcium carbonate was controlled by adding different crystal-shape-forming additives. Effects of sodium hexametaphosphate, zinc chloride, sodium tetraborate decahydrate, and aluminium chloride on the crystal shape of precipitated calcium carbonate were studied. The effects of crystal-shaped additives of precipitated calcium on the whiteness of modified fly ash and hand sheets were analyzed. The results showed that the addition of ZnCl₂ (0.35%) can play a role in coating fly ash well. The coating effect of the acicular, chain, and lamellar precipitated calcium carbonate on the surface of fly ash was slightly less effective than that of globular crystals.

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Keywords: Fly ash; Precipitated calcium carbonate; Crystal-shaped additives; Whiteness

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INTRODUCTION

Fly ash is a by-product generated due to the combustion of pulverized coal (Mahantayya et al. 2022). In recent years, a large amount of fly ash has accumulated globally, which is an environmental hazard. If not disposed properly, people’s health and the environment will be in danger (Li et al. 2016; Zhao 2016; Xu et al. 2019). Realizing the comprehensive utilization of fly ash is beneficial to reduce the environmental hazard. About 780 million tons of fly ash is globally produced per year, but only about 17 to 20% is utilized. The major utilization of fly ash is either in the production of Portland pozzolana cement used as a building material, or in soil stabilization (Singh et al. 2010; Ondova and Stevulova 2012; Mahantayya et al. 2022). Moreover, recent research works show its potential utilization in the papermaking industry (Fan et al. 2015, 2016; Wang 2015). Fly ash can be used as filler because its chemical composition and particle morphology are similar to kaolinite filler (Liu 2010; Li et al. 2022). It can react with water to produce a cementitious substance that has the certain strength. Because the microstructure of fly ash has large pores and is loose, it has excellent adsorption activity, which has a basis for the modification of fly ash (Li et al. 2022).

The color of fly ash is mostly gray to black, which affects the whiteness of fly ash (Wang 2015; Xu et al. 2021). Fu et al. (2007) used fly ash in corrugated paper with low whiteness requirements. Wang (2015) calcined the fly ash and processed the fly ash with acid, and the whiteness of fly ash increased to 53 %ISO.

There has been a lot of research on the modification of fly ash to increase whiteness. Most research focused on traditional physical and chemical methods. There is also a
surface coating modification method (Fu et al. 2007). However, coating fly ash with weak shear resistance is not effective, since the underlying substance is easy to be exposed in the process of papermaking and affects the paper whiteness. Fan et al. (2015) modified fly ash in the Ca(OH)₂—H₂O—CO₂ system with a single-tube ventilation device. Their research concluded that modified fly ash had great advantages in paper physical strength. However, crystal morphology of precipitated calcium carbonate coated on the surface of fly ash has not been studied. Fan et al. (2016) researched how the crystal shape of precipitated calcium carbonate affected the whiteness of modified fly ash. The study was not particularly focused on a controlled crystal shape of precipitated calcium carbonate during the coating process. The preparation method of precipitated calcium carbonate with different crystal shapes has been introduced (Gu et al. 1993; Wang 2007; Zeng et al. 2009; Yu 2016; Liu 2021).

The morphology of precipitated calcium carbonate was controlled by adding different crystal-shaped additives in this work. The effects of sodium hexametaphosphate, zinc chloride, sodium tetraborate decahydrate, and aluminium chloride on the crystal shape of precipitated calcium carbonate were studied. The effect of crystal-shaped additives of precipitated calcium carbonate on the whiteness of modified fly ash and hand sheets were then analyzed.

**EXPERIMENTAL**

**Materials**

Fly ash was supplied from Guangzhou Paper Group Co., Ltd. (Guangzhou, China). Calcium oxide and carbon dioxide were 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, of which the pore sizes were 75, 60, 50, 46.15, 37.5, 30, 25, 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 (calcium hydroxide concentration was 7%), then specified components were added to the mixture for 10 min under stirring at 500 rpm. Carbon dioxide was bubbled into the mixture. When the suspension reached pH 7, the experiment was considered complete.

*Paper preparation with modified fly ash as filler*

The bleached eucalyptus pulp was diluted to 0.3% using tap water, and modified fly ash (based on slurry) were added during handsheet making. The mixture was dispersed by a GBJA fiber standard disintegrator (Nanjing Shounuo Instrument Co., Ltd., Nanjing, China), and 0.05% CPAM (based on dry pulp) was added as a retention aid. The handsheets
were formed using a Rapid-Köthen Sheet former (RK3AKWT; Austria PTI Ltd., Vienna, Austria) at a filler ratio of 25% and basis weight of approximately 72 g/m².

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 (Elrepho 070, L&W, Kista, Sweden) 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 (SC-701MKII, Sanyu, Tokyo, Japan model; Full Manufacturer Name, City, Country). Samples were observed using an EVO 18 Special Edition scanning electron microscope (Carl Zeiss, Oberkochen, Germany) operating at an accelerating voltage of 10.0 kV.

RESULTS AND DISCUSSION

Effects of Sodium Hexametaphosphate
As shown in Table 1, as the increase of sodium hexametaphosphate, the whiteness of the modified fly ash and paper were improved. The whiteness of modified fly ash was far higher than the original fly ash, which was 25.1% ISO. When the mass of sodium hexametaphosphate was 0.1% (based on the mass of calcium carbonate generated by the reaction), the whiteness of modified fly ash and paper slightly increased compared with that of modified fly ash without sodium hexametaphosphate added. Figure 1 shows that the surface of fly ash was coated with many large particles, which may fall off due to external shear in the process of papermaking. When the mass of sodium hexametaphosphate was 0.15%, and the amount of large calcium carbonate self-polymerization on the surface of modified fly ash was decreased, precipitated calcium carbonate with acicular shape exhibited even distribution on the surface of modified fly ash, and irregular crystal may cause generation of thick and uneven fly ash layer. Finally, the whiteness of modified fly ash is affected compared with 0.1% sodium hexametaphosphate added.

Table 1 shows that the whiteness of modified fly ash was improved with the increased mass of sodium hexametaphosphate from 0.2% to 0.3%.

Table 1. Effect of Sodium Hexametaphosphate (H7NaO18P6) as Crystal-shaped Additive on Whiteness of Modified Fly Ash and Paper

<table>
<thead>
<tr>
<th>M\text{H}<em>7\text{NaO}</em>{18}\text{P}_6 (%)</th>
<th>Whiteness of Modified Fly Ash (%ISO)</th>
<th>Whiteness of Paper (%ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.27</td>
<td>72.64</td>
</tr>
<tr>
<td>0.10</td>
<td>62.33</td>
<td>72.77</td>
</tr>
<tr>
<td>0.15</td>
<td>62.79</td>
<td>73.45</td>
</tr>
<tr>
<td>0.20</td>
<td>64.01</td>
<td>74.66</td>
</tr>
<tr>
<td>0.25</td>
<td>64.67</td>
<td>74.89</td>
</tr>
<tr>
<td>0.30</td>
<td>61.34</td>
<td>72.01</td>
</tr>
</tbody>
</table>
When the mass of sodium hexametaphosphate was 0.25%, the whiteness of modified fly ash and paper reached the maximum (64.7% ISO and 74.9% ISO, respectively), which increased by 2.4% ISO compared with no sodium hexametaphosphate addition. When the mass of sodium hexametaphosphate was 0.25%, precipitated calcium carbonate with acicular shape was well formed, and crystal particles were relatively uniform. However, the increase in whiteness of modified fly ash and paper was not so obvious. This indicated that acicular crystals may have been interlaced with each other and the fly ash was easy to expose due to the unfirm coating in the process of crystal growth on the surface of fly ash. While the uniform coating layer was relatively thin, the coating performance was not so ideal.

![Figure 1](image)

**Fig. 1.** SEM images of modified fly ash coated with precipitated calcium carbonate controlled by sodium hexametaphosphate  
(a) The mass of sodium hexametaphosphate was 0.1%;  
(b) The mass of sodium hexametaphosphate was 0.15%  
(c) The mass of sodium hexametaphosphate was 0.2%  
(d) The mass of sodium hexametaphosphate was 0.25%  
(e) The mass of sodium hexametaphosphate was 0.3%

**Effects of Zinc Chloride**

As shown in Table 2, the whiteness of modified fly ash was far higher than the original fly ash, which was 25.12% ISO. When the mass of zinc chloride was 0.2% (based on the mass of calcium carbonate generated by the reaction), the whiteness values of modified fly ash and paper were decreased. The surface of the modified fly ash was covered by a large number of precipitated calcium carbonate aggregates with irregular shape.
As can be seen from Fig. 2, when the mass of zinc chloride was 0.25%, a small number of precipitated calcium carbonate with globular crystals was presented, and there were also a large number of rod-like crystals. When the mass of zinc chloride increased from 0.25% to 0.3%, the whiteness of modified fly ash and filling paper was improved. As shown in Fig. 2, the globular crystal particles increased gradually with the increase of zinc chloride, the shape of calcium carbonate on the surface of fly ash gradually changed from irregular to globular.

When the mass of zinc chloride was 0.35%, the whiteness of modified fly ash and paper reached the maximum (65.33 %ISO and 75.59 %ISO, respectively). Figure 2 shows that the surface of the fly ash was uniformly coated with a layer of globular crystal, which improved the whiteness and coating effect of the modified fly ash. However, with the increase of zinc chloride mass to 0.4%, the whiteness of modified fly ash decreased, and there was almost the same effect with no zinc chloride added. Therefore, when the mass of zinc chloride was 0.35%, it was capable of controlling the form of uniform globular precipitated calcium carbonate compared with acicular precipitated calcium carbonate. The whiteness of modified fly ash coated by globular crystal was slightly better than that of acicular crystal. This may have been due to the globular crystal layer being firmer than the acicular crystal layer.

**Fig. 2.** SEM images of modified fly ash coated with precipitated calcium carbonate controlled by zinc chloride
a) The mass of zinc chloride was 0.2%;
b) The mass of zinc chloride was 0.25%;
c) The mass of zinc chloride was 0.3%;
d) The mass of zinc chloride was 0.35%;
e) The mass of zinc chloride was 0.4%;
Table 2. Effect of Zinc Chloride (ZnCl$_2$) as Crystal Shape Additive on Whiteness of Modified Fly Ash and Paper

<table>
<thead>
<tr>
<th>M ZnCl$_2$ (%)</th>
<th>Whiteness of Modified Fly Ash (%ISO)</th>
<th>Whiteness of Paper Filled with Modified Fly Ash (%ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.27</td>
<td>72.64</td>
</tr>
<tr>
<td>0.20</td>
<td>61.85</td>
<td>72.07</td>
</tr>
<tr>
<td>0.25</td>
<td>62.91</td>
<td>73.69</td>
</tr>
<tr>
<td>0.30</td>
<td>64.12</td>
<td>74.22</td>
</tr>
<tr>
<td>0.35</td>
<td>65.33</td>
<td>75.59</td>
</tr>
<tr>
<td>0.40</td>
<td>62.41</td>
<td>72.69</td>
</tr>
</tbody>
</table>

Effects of Sodium Tetraborate Decahydrate

As shown in Table 3, the whiteness of modified fly ash was far higher than the original fly ash, which was 25.1% ISO. When the addition of sodium tetraborate decahydrate increased from 0.25% to 0.3% (based on the mass of calcium carbonate generated by the reaction), the whiteness of modified fly ash and paper was slightly improved. Combined with Fig. 3, it can be seen that the surface of fly ash was coated with precipitated calcium carbonate, which was lamellar shape, and there were some irregular crystal particles. It was noted that the size of calcium carbonate particles crystallized on the surface of fly ash was large.

Fig. 3. SEM images of modified fly ash coated with precipitated calcium carbonate controlled by sodium tetraborate decahydrate
a) The mass of sodium tetraborate decahydrate was 0.25%;
b) The mass of sodium tetraborate decahydrate was 0.3%;
c) The mass of sodium tetraborate decahydrate was 0.35%;
d) The mass of sodium tetraborate decahydrate was 0.4%;
e) The mass of sodium tetraborate decahydrate was 0.45%;
Table 3. Effect of Sodium Tetraborate Decahydrate (Na₂B₄O₇·10H₂O) as Crystal-shaped Additive on Whiteness of Modified Fly Ash and Paper

<table>
<thead>
<tr>
<th>M_{Na₂B₄O₇·10H₂O} (%)</th>
<th>Whiteness of Modified Fly Ash (%ISO)</th>
<th>Whiteness of Paper (%ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.27</td>
<td>72.64</td>
</tr>
<tr>
<td>0.25</td>
<td>62.51</td>
<td>72.70</td>
</tr>
<tr>
<td>0.30</td>
<td>62.86</td>
<td>72.88</td>
</tr>
<tr>
<td>0.35</td>
<td>63.00</td>
<td>73.09</td>
</tr>
<tr>
<td>0.40</td>
<td>63.85</td>
<td>73.56</td>
</tr>
<tr>
<td>0.45</td>
<td>62.22</td>
<td>73.33</td>
</tr>
</tbody>
</table>

It is possible that a few of the crystal shape additives cannot achieve the goal of controlling the crystal shape and particle size. In contrast, the precipitated calcium carbonate with lamellar shape existed laterally on the surface of fly ash with crystal cladding layer spreading, so it has an advantage to cover the fly ash by lamellar crystal particles. However, as a result of large particle size and attachment through physical adsorption, the crystallization stability may be poor. When the mass of sodium tetraborate decahydrate was 0.4%, the whiteness of modified fly ash and paper reached the maximum (63.8 %ISO and 73.6 %ISO, respectively). It can be noticed that the modified fly ash surface was covered by the crystal particles with various particle sizes in the way of longitudinal stretching. In other words, the precipitated calcium carbonate shared a single crystal face, which greatly reduced surface energy and made modified fly ash more stable. When the mass of sodium tetraborate decahydrate was 0.45%, that shape of precipitated calcium carbonate on the surface of fly ash was irregular, and there was also a small amount of massive calcium carbonate self-polymers, which may be caused by the high concentration of sodium tetraborate decahydrate. It did not make any difference in controlling the crystal shape, and the state of the whole reaction system was affected, resulting in the agglomeration of precipitated calcium carbonate. Therefore, compared with sodium hexametaphosphate and zinc chloride, sodium tetraborate decahydrate may have a weaker control over the nucleation growth rate of calcium carbonate crystals on the surface of fly ash, so the large lamellar crystal particles and irregular coating were shown.

Effects of Aluminium Chloride

As shown in Table 4, when the mass of aluminium chloride increased from 0.05% to 0.15%, the whiteness of modified fly ash and paper was improved. Additionally, the whiteness of modified fly ash was far higher than the original fly ash, which was 25.1 %ISO. As shown in Fig. 4, when the mass of aluminium chloride was 0.05%, the shape of precipitated calcium carbonate was irregular. When the mass of aluminium chloride was 0.10%, the surface of fly ash was covered with globular crystal particles, and there were also some irregular calcium carbonate self-copolymers. When the mass of aluminium chloride was 0.15%, the size of globular crystal particles on the surface of fly ash decreased compared with that of 0.10% aluminium chloride. However, there was an increase in irregular calcium carbonate self-polymers. Compared with addition of ZnCl₂, aluminium chloride can also control calcium carbonate shape to form the globular crystal particles under the condition of low addition. Further, there were more precipitated calcium carbonate self-polymers that covered the surface of modified fly ash. Because the small amount of AlCl₃ was not enough to connect small size precipitated calcium carbonate, it
was shown contrastingly, that crystal growth was inhibited and caused small particles size. This means calcium carbonate surface energy increased. The whiteness of the modified fly ash and paper reached the maximum (63.7 %ISO and 74.1 %ISO, respectively) when the mass of aluminium chloride was 0.20%, which increased 1.45 %ISO compared with no addition of aluminium chloride. As shown in Fig. 4, the surface of the fly ash was covered with a layer of chain crystal particles that were interwoven with each other. The whiteness of modified fly ash was not greatly improved because the surface of fly ash could be exposed due to gaps in the interweaving process, and the crystal size was large, which may have poor shear resistance. As shown in Table 4, the whiteness of modified fly ash decreased when the mass of aluminium chloride was 0.25%, which was even lower than the whiteness of modified fly ash obtained without the addition of aluminium chloride. As depicted in Fig. 4, a globular-shaped layer of precipitated calcium carbonate with small particle size was crystallized on the surface of fly ash; there were also some large particle size polymers. A large amount of Al(OH)₃ was generated in the solution via the reaction of aluminum chloride with water, which led to an increase in the concentration of Al(OH)₃. Because of its binding effect, calcium carbonate crystal particles that were precipitated during crystallization on the surface of fly ash were hampered by Al(OH)₃. Moreover, a large conglomeration formed by calcium carbonate crystal bonding, as shown in the Fig. 4.

![Fig. 4. SEM images of modified fly ash coated with precipitated calcium carbonate controlled by aluminium chloride](image-url)

- a) The mass of aluminium chloride was 0.05%;
- b) The mass of aluminium chloride was 0.1%;
- c) The mass of aluminium chloride was 0.15%;
- d) The mass of aluminium chloride was 0.2%;
- e) The mass of aluminium chloride was 0.25%;
Table 4. Effect of Aluminium Chloride (AlCl₃) as Crystal Shape Additive on Whiteness of Modified Fly Ash and Paper

<table>
<thead>
<tr>
<th>M AlCl₃ (%)</th>
<th>Whiteness of Modified Fly Ash (%ISO)</th>
<th>Whiteness of Paper (%ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62.27</td>
<td>72.64</td>
</tr>
<tr>
<td>0.05</td>
<td>62.44</td>
<td>72.79</td>
</tr>
<tr>
<td>0.10</td>
<td>63.10</td>
<td>73.59</td>
</tr>
<tr>
<td>0.15</td>
<td>63.57</td>
<td>73.91</td>
</tr>
<tr>
<td>0.20</td>
<td>63.72</td>
<td>74.06</td>
</tr>
<tr>
<td>0.25</td>
<td>59.85</td>
<td>70.13</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Compared with the four treatment methods, the addition of zinc chloride can play a role in coating fly ash well and precipitated calcium carbonate with globular shape. In addition, the whiteness of the modified fly ash filler paper obtained was greatly improved.

1. With increased addition of sodium hexametaphosphate, the crystal shape of precipitated calcium carbonate was acicular. When the mass of sodium hexametaphosphate was 0.25%, modified fly ash was coated by precipitated calcium carbonate with acicular shape, and the whiteness of modified fly ash and paper reached the maximum of 64.7 %ISO and 74.9 %ISO, respectively, which increased by 2.4 %ISO compared to no addition of sodium hexametaphosphate.

2. With increased addition of zinc chloride, the crystal shape of precipitated calcium carbonate was globular. When the mass of zinc chloride was 0.35%, modified fly ash was coated by precipitated calcium carbonate with acicular shape. The whiteness of modified fly ash and paper reached the maximum of 65.3 %ISO and 75.6 %ISO, respectively, which was 3.1 %ISO more than that of modified fly ash without zinc chloride added.

3. As the addition of sodium tetraborate increased, the crystal shape of precipitated calcium carbonate was lamellar. When the mass of sodium tetraborate was 0.4%, modified fly ash was coated by precipitated calcium carbonate with lamellar shape and the whiteness of modified fly ash and paper reached the maximum of 63.8 %ISO and 73.6 %ISO, respectively, which was 1.58 %ISO more than that of modified fly ash without sodium tetraborate added.

4. With increased addition of aluminium chloride, the crystal shape of precipitated calcium carbonate was chain-like. When the mass of aluminium chloride was 0.2%, modified fly ash was coated by precipitated calcium carbonate with chain shape and the whiteness of modified fly ash and paper reached the maximum of 63.7 %ISO and 74.1 %ISO, respectively, which was 1.45 %ISO more than that of modified fly ash without aluminium chloride added.

5. Therefore, the addition of 0.35% zinc chloride can play a role in coating fly ash well and precipitated calcium carbonate with globular shape. While precipitated calcium carbonate with acicular shape with the addition of sodium hexametaphosphate and chain-shaped crystals with aluminium chloride addition exhibits an interwoven effect.
on the surface of fly ash, pores between precipitated calcium carbonate crystals were seen. In addition, because the size of lamellar precipitated calcium carbonate with sodium tetraborate addition was uneven, the crystals on the fly ash surface exhibited a disordered coating state. Thus, the coating effect with the acicular, chain, and lamellar precipitated calcium carbonate on the surface of fly ash was not much more effective than that of globular.

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