Effect of Calcium Hydroxide Concentration and Stirring Rate on the Crystallization of the Calcium Carbonate on the Surface of Fly Ash

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To improve the whiteness of fly ash, fly ash was prepared using calcium hydroxide, water, and carbon dioxide as the reaction system to coat calcium carbonate crystals on the surface of the fly ash. This study investigated the effect of the calcium hydroxide content and stirring rate on the crystallization of the calcium carbonate on the fly ash surface. The results showed that the calcium carbonate nanoparticles prepared with a 7% calcium hydroxide concentration and stirring rate of 500 rpm were coated on the surface of the fly ash, and the whiteness of the modified fly ash reached a maximum of 59.7% ISO. The microscopic process of heterogeneous nucleation of calcium carbonate and the LaMer model were explored to explain the influence of the precursor reactant concentration and stirring rate on the nucleation and growth of the crystal.

Keywords: Heterogeneous nucleation; Fly ash; LaMer model; Calcium carbonate

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INTRODUCTION

Fly ash is one of the largest sources of solid waste emissions in China. The accumulation of fly ash can directly or indirectly cause a series of environmental problems in the atmosphere, soil, and rivers, and at the same time contribute to the waste of resources (Hemalatha and Ramaswamy 2017). The main components of fly ash are oxides of silicon, aluminum, and iron, which have physical and chemical properties similar to the fillers used in papermaking. Therefore, fly ash has its own advantages as a filler in papermaking (Wu *et al.* 2013). However, because of the low whiteness of fly ash, its applications in the paper industry are limited. Calcium carbonate has a relatively high whiteness and is a fairly cheap material. Therefore, in recent years, a number of researchers have modified fly ash with calcium carbonate to increase the whiteness, thereby increasing the application of fly ash in papermaking. Most research has focused on coating calcium carbonate on the fly ash surface with uniform crystal nucleation. Fan (2004) added three mineral powders (calcium carbonate, wollastonite, and dolomite) to the $Ca(OH)_2$-H_2O-CO_2 system to react $Ca(OH)_2$ with CO_2. The generated nano-calcium carbonate particles underwent heterogeneous nucleation growth on the surface of the mineral powder to create modified powders. Through visual observation, it was determined that the surface of the modified powder particles was coated with a nanometer calcium carbonate layer that was coarser than the unmodified powder.

The mechanism of crystal nucleation and growth in aqueous solutions is not fully understood. In recent years, some studies have used the multi-dispersion hard-ball model

(Cacciuto *et al*. 2004). In this paper, a new microscopic model was used, in which the solute granules were treated as equal-diameter spheres in the dimer formation at the onset of homogenous nucleation. During the crystal growth process, seed crystals and solute granules formed. Considered to be unequal diameter spheres, large spheres represent seed crystals and small spheres represent solute particles (Wang 2007). These model theories can be used to explain and analyze the heterogeneous nucleation of calcium carbonate.

In this paper, calcium hydroxide was used as the raw material, whereas fly ash, which had the carbon and magnetic iron removed, was used as the substrate. Carbon dioxide was introduced to the reaction system, and the fly ash surface was used as the substrate. There was good coverage by the well dispersed calcium carbonate crystals. The distribution of the particle size can be adjusted with the calcium hydroxide concentration, and the dispersion quality can be adjusted by changing the crystal control agent concentration to adjust the crystal growth shape, thereby achieving better coating effects. Additionally, this study used the LaMer model as a reference standard and combined the microscopic process of heterogeneous nucleation and crystallization to provide a theoretical explanation and guidance for the nucleation and growth of calcium carbonate on the fly ash surface.

EXPERIMENTAL

Materials

The fly ash was provided by Guangzhou Paper Group Co., Ltd. (Guangdong, China). The surface area of the fly ash is 7.06 g/m^2. The calcium oxide and carbon dioxide were provided by Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China).

Fly ash is generally considered to contain three different types of constituents: crystalline minerals, unburnt carbon particles, and non-crystalline aluminosilicate glass (Ward and French 2005). With the help of the X-ray diffraction technique available, it was determined that the FA mainly was composed of calcite, calcium feldspar, and quartz, which is shown in Fig. 1.

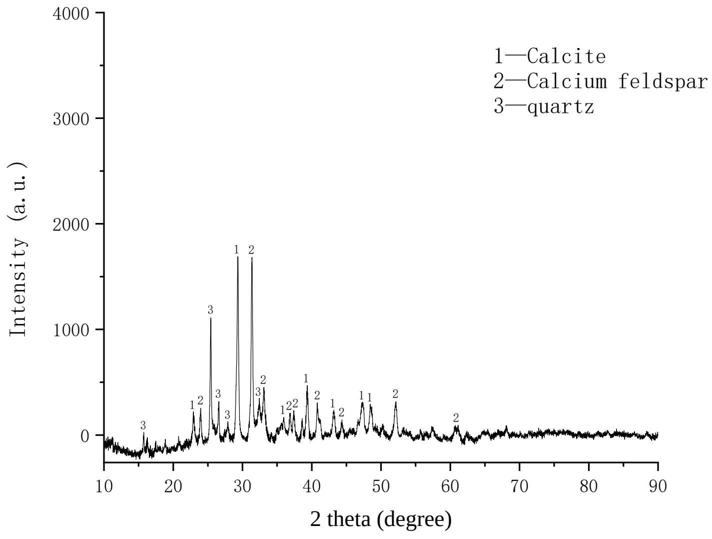

Fig. 1. Raw fly ash XRD pattern

Methods

Analytical method

An X-ray diffractometer (D8 Discover Plus, Dresden, Deutschland) was used to measure constituents of the fly ash. An L&W whiteness meter (ELREPHO 070, Kista, Sweden) was used to assess the whiteness of the fly ash modified, according to the national standard (GB/T 23774-2009). The instrument was first calibrated using a standard white board, and then the whiteness test of the powder particles was conducted. After filling the powder sampler under the same test conditions and rotating the sample angle, the results of three consecutive measurements with differences not exceeding 0.3 were recorded. The average of the three determination results were used as the whiteness value of the sample.

Heterogeneous nucleation of the basic fly ash

First, an amount of quick lime was digested at 85 °C for 1 h. After digestion was completed and the substance cooled, the bottom residue was filtered to obtain a calcium hydroxide suspension, and the solid content was further used. A calcium hydroxide suspension with a 500-mesh fly ash ratio of 1:1 and various concentrations of calcium hydroxide suspension was uniformly mixed with the fly ash in a bubble carbonization apparatus (made by ourselves) at different stirring speeds. The details are shown in Tables 1 and 2. For approximately 10 min, carbon dioxide gas was passed through the bottom of the device at 0.1 L/min and the reaction was started. The pH of the reaction solution was monitored in real time with a pH meter. When the pH was 7, the reaction was terminated and modified pulverized coal was generated. The ash composite was separated into containers, allowed to stand for 30 min, and then dried in an oven to obtain a modified fly ash filler.

Table 1. Reactant Calcium Hydroxide Concentration

Reaction Condition	Reactant	Amount (%)						
500 rpm/min	$Ca(OH)_2$ Concentration	3%	5%	7%	10%	15%	20%	25%

Table 2. Reactant Condition Stirring Speeds

Reactant	Reaction Condition	Speed (rpm/min)						
7%	Stirring Speed	0	200	300	400	500	600	700

RESULTS AND DISCUSSION

Whiteness

Effect of the calcium hydroxide concentration

The effect of calcium hydroxide on the whiteness of the modified fly ash was determined at a stirring rate of 500 rpm under constant conditions. Table 3 shows that the whiteness tendency of the modified fly ash increased and then decreased as the calcium hydroxide concentration increased. The main reason for this trend was that when the concentration of calcium hydroxide was low, the solid content of the reaction liquid was relatively low after it was uniformly mixed with the fly ash. At a concentration of 7% calcium hydroxide, the whiteness of the modified fly ash reached a maximum of 59.7%

ISO. Because the first step in this reaction was the dissolution of calcium hydroxide solid particles and carbon dioxide gas in the solution through a hydrolysis reaction, the second step was Ca^{2+} reacting with CO_3^{2-} to generate calcium carbonate. Therefore, the lower reactant concentration favored the dissolution of calcium hydroxide solids and uniform mass transfer dissolution of carbon dioxide in the reaction liquid under stirring. In contrast, when the calcium hydroxide concentration was within a relatively low range after homogeneous mixing with the fly ash, the fly ash was a porous substance with strong adsorption. The Ca^{2+} in the solution immediately adsorbed onto the surface of the fly ash when the carbon dioxide was hydrolyzed to generate CO_3^{2-}. The combination of Ca^{2+} on the fly ash surface facilitated the crystallization of calcium carbonate on the surface of the fly ash to form a uniform coating. However, when the concentration of calcium hydroxide was too low, the concentration of the reactants was low after mixing with the fly ash particles and the sedimentation velocity of the solids was fast. This may have caused part of the solid particles to remain during the modification process, even if they rely on external agitation for mixing. There was the possibility of sedimentation, which inhibited the fly ash coating process when the reactant concentration was too low. When the Ca^{2+} on the surface of the fly ash was saturated, there was free Ca^{2+} in the solution. When carbon dioxide was introduced, it reacted with CO_3^{2-} to generate calcium carbonate. As the free calcium carbonate molecules reached supersaturation, crystals were precipitated. Theoretically, heterogeneous nucleation coating occurred with fly ash as the precursor particles, but because the reactant concentration was too low, the probability of contact with the fly ash was greatly reduced; therefore, it was easy for independent nucleation to occur in the solution. As the reaction proceeded, free calcium carbonate nuclei grew continuously. When the calcium hydroxide concentration was high, the concentration of the reactants was higher after mixing with the fly ash, which caused the dissolution of the calcium hydroxide and the hydrolysis of the carbon dioxide to be suppressed to some extent. Additionally, the movement of the calcium carbonate molecules generated by the reaction was affected. When the surface of the fly ash crystal was coated with calcium carbonate-wrapped calcium hydroxide, the formation of large particles mixed with the fly ash after the reaction was extensive, especially when the concentration of calcium hydroxide exceeded 20%. Under the same conditions, the concentration of the reactants was higher and the supersaturation time of the calcium carbonate crystals in the solution was shorter, so that at the same carbon dioxide feed rate, the calcium carbonate crystals self-crystallized under high concentrations of reactants and the probability of this phenomenon was greater. Therefore, an appropriate calcium hydroxide concentration is crucial for the fly ash modification process.

Table 3. Effect of Different $Ca(OH)_2$ Concentrations on the Fly Ash Whiteness

$Ca(OH)_2$ Concentration	3%	5%	7%	10%	15%	20%	25%
Modified Fly Ash Whiteness (ISO)	56.84 (0.92)	57.45 (0.94)	59.70 (0.92)	58.19 (0.97)	57.02 (0.89)	55.23 (0.91)	53.07 (1.05)

Noting: the data in parentheses represents the values of standard deviation

Effect of the stirring rate

The effect of the stirring rate in the reactor on the whiteness of the modified fly ash was determined under unchanging reaction conditions and a 7% calcium hydroxide concentration. The change in the whiteness of the fly ash after modification can be seen in Table 4. With an increase in the stirring speed, the whiteness of the modified fly ash first increased and then decreased. At a stirring rate of 500 rpm, the whiteness of the modified fly ash reached a maximum of 59.70 ISO, whereas the whiteness of the modified fly ash was only 45.2% ISO without stirring. This may have been because of the fact that the calcium hydroxide suspension cannot be fully mixed with the fly ash particles without agitation. In the carbonization modification process, carbon dioxide was not uniformly mass-transferred when it was added into the system from the bottom, which resulted in pulverized coal generation. A large amount of heavy calcium carbonate crystallized on the surface of the ash, and some of the fly ash was not coated with surface crystals. In contrast, the critical partial supersaturation was exceeded because of the instantaneous precipitation of large amounts of calcium carbonate crystals in parts of the system. The degree and occurrence of the self-crystallization phenomenon of calcium carbonate eventually resulted in a low whiteness of the modified fly ash. The stirring action can promote the mass transfer of carbon dioxide in the process of carbonization modification, and it is easier to break the carbon dioxide bubbles into a large number of smaller bubbles so that the mass transfer area of carbon dioxide in the solution increases, which is favorable for the dissolution of calcium hydroxide. This process promotes the nucleation of calcium carbonate. When the stirring speed was low, the mass transfer rate of carbon dioxide was low and the supersaturation degree of the calcium carbonate in the local position was high. This resulted in the partial crystallization of the fly ash surface, which caused the crystal growth to become unstable. It was easy for the growth to fall from the surface of the fly ash and form independent calcium carbonate that underwent self-polymerization. The body was not able to uniformly coat the fly ash precursor particles. When the stirring speed was high, it accelerated the mass transfer rate of the carbon dioxide gas, which prevented the supersaturation of the local calcium carbonate crystal from exceeding the critical supersaturation of the heterogeneous nucleation and the self-crystallization phenomenon. This made the calcium carbonate crystal in the fly ash stable, which then nucleated. However, when the stirring speed was too high, the theory of molecular motion in physics became relevant. The faster a particle moves, the greater the chance of collision between particles, which increases the probability of particle-to-particle binding. When particle-to-particle binding was strong, calcium carbonate crystals collided with each other, which caused self-polymerization when the calcium carbonate crystals were precipitated. Therefore, choosing the proper stirring speed has an important influence on the crystalline coating modification of fly ash.

Table 4. Effect of the Stirring Rate on the Fly Ash Whiteness

Stirring Speed (rpm)	0	200	300	400	500	600	700
Modified Fly Ash Whiteness (ISO)	45.35 (0.93)	52.14 (1.10)	54.87 (1.08)	58.19 (0.98)	59.70 (0.99)	55.52 (1.13)	53.43 (1.02)

Noting: the data in parentheses represents the values of standard deviation

Microcrystallization Analysis

Reaction principle analysis

The coating of calcium carbonate crystals on the fly ash surface used the chemical reaction of calcium hydroxide and carbon dioxide to form a coating layer of calcium carbonate. This controlled the reaction conditions so that the newly formed calcium carbonate crystals were on the surface of the fly ash particles in the solution. The nucleation, growth, and coating were grown on the fly ash master granules. The reaction system was the $Ca(OH)_2$-H_2O-CO_2 system. The main chemical reactions in the system were:

$$Ca(OH)_2(s) \rightarrow Ca^{2+}\,(aq) + 2OH^{-}\,(aq) \tag{1}$$

$$CO_2(g) \rightarrow CO_2\,(aq) \tag{2}$$

$$CO_2\,(aq) + OH^{-}\,(aq) \rightarrow HCO^{3-}\,(aq) \tag{3}$$

$$HCO^{3-}\,(aq) + OH^{-}\,(aq) \rightarrow H_2O + CO_3^{2-}\,(aq) \tag{4}$$

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow CaCO_3\,(s) \tag{5}$$

The last three steps (Eqs. 3 to 5) in the reaction are transient reactions that were completed instantaneously. The control reaction process was mainly the dissolution process of calcium hydroxide and the absorption process of carbon dioxide. The nucleation growth of calcium carbonate crystals was as follows:

$$Ca^{2+} + CO_3^{2-} \rightarrow D1 \tag{6}$$

$$D1 + Ca^{2+} \rightarrow D1\,Ca^{2+} \tag{7}$$

$$D1\,Ca^{2+} + CO_3^{2-} \rightarrow D2 \tag{8}$$

When calcium and carbonate ions were present in the solution, they combined to form calcium carbonate molecules. Numerous calcium carbonate molecules were formed to reach the saturation point of calcium carbonate in the solution and precipitate calcium carbonate crystals.

Reaction process analysis

In the solution without other external solids, the solid $CaCO_3$ formed mainly went through four stages of movement, including molecular polymerization, crystal nucleus, and crystal growth, as is shown in Fig. 2. The process took place under the influence of mutual conversion. Specifically, after the start of the reaction, as a result of the collision of $CaCO_3$ molecules (motion unit) in a short period of time, the new intermediates emerged initially as gel-state metastable linear molecules, which resulted in a substantial increase in the viscosity of the suspension. When the number of molecules in this molecular polymer reached a certain amount, crystal nuclei began to form. The general nuclei remained unstable, and only when the crystal nuclei continued to grow did they become stable crystal particles (Department of Personnel Education 1997). Assuming that a single calcium carbonate crystal was an equal-diameter sphere, a substantial secondary reaction took place from the beginning of the formation of the molecular polymer to the formation of the nucleus. The calcium carbonate molecules in the solution had a low concentration because of the start of the reaction. Generally, two equal-diameter balls first collided, and a dimerization reaction occurred. Then, as the concentration of calcium carbonate molecules increased, formation of trimers, tetramers, and other reactions occurred, as is shown by Eq. 9. The growth reaction from the crystal nuclei to crystals generally began to transition to the first order reaction. As is shown by Eq. 10, the concentration of calcium carbonate in the solution was mainly used as power for crystal growth because the diameter of the generated crystal nuclei was large.

$$U_n = -\mathrm{dC} / \mathrm{dt} = K_n C^2 \tag{9}$$

$$U_g = -\mathrm{dC} / \mathrm{dt} = K_g C \tag{10}$$

where K_n (S^{-1}) and K_g ($L\cdot mol^{-1}\cdot S^{-1}$) represent the chemical reaction rate constants respectively (Wang 2007).

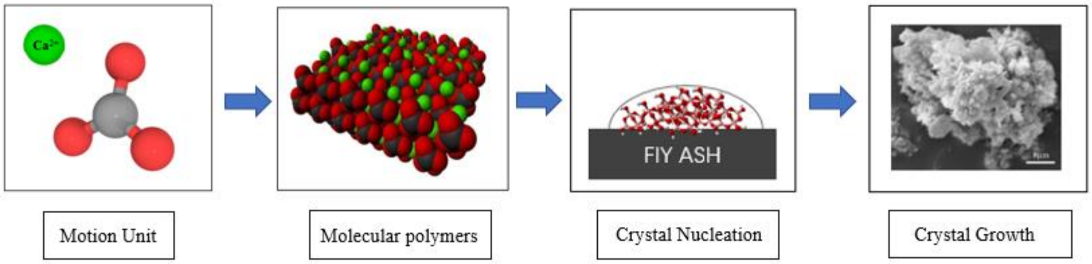

Fig. 2. Microscopic process of the calcium carbonate crystallization and growth on the fly ash surface

LaMer model analysis

Using the LaMer model (LaMer and Dinegar 1950; LaMer 1952; Deng *et al*. 2012), which is shown in Fig. 3, the process of crystal nucleation of calcium carbonate crystals on the fly ash surface was theoretically analyzed. Crystallization was considered a reaction crystallization process in this paper, and its driving force was the solubility of the calcium carbonate.

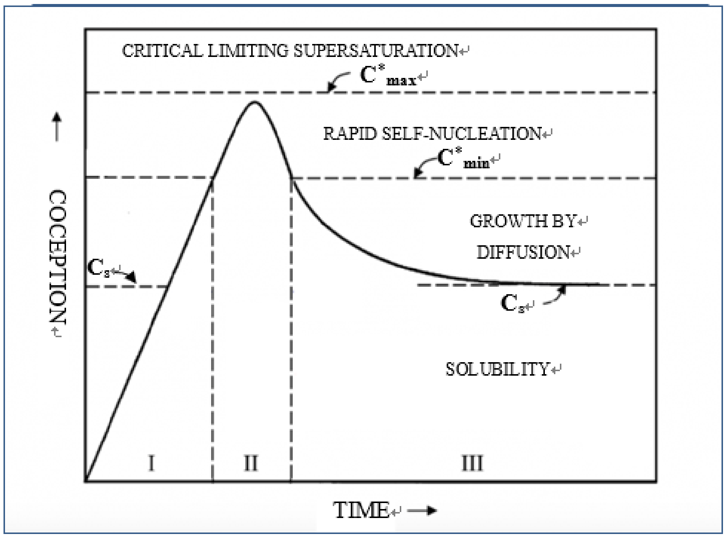

Fig. 3. LaMer model of the monodisperse particles

When a saturated solution of calcium carbonate was not reached as the reaction progressed, the concentration of calcium carbonate molecules increased until it reached its saturation point (C_s). As the reaction progressed, the calcium carbonate solution became supersaturated, and the solution was in a metastable state. In the homogeneous nucleation system, the nucleation barrier was high because of spontaneous nucleation and did not start to form (Fan *et al.* 2003). Nucleation occurred until the calcium carbonate molecular concentration reached C^*_{min}, which is the so-called critical nucleation concentration, where nucleation begins. In phase II, a large number of nuclei were generated, so that the concentration of the solution began to rapidly drop to the C^*_{min} position. In phase III, there were no more new nuclei generated, only the growth of previously existing nuclei.

In the heterogeneous nucleation system, because of the presence of the external material fly ash, the nucleation barrier was greatly reduced and primary nucleation occurred on the surface of the substrate by heterogeneous nucleation. In the mixed state, it was important to crystallize the precipitate. To more uniformly coat the crystalline surface of the fly ash, this local supersaturation must be changed. According to the contribution of the main flow of the entire flow field to the local average of the concentration of each substance, from the perspective of macro-mixing, the crystallizer can be divided into three regions. The first is the feeding region, where rapid reactions produce high local supersaturation and preliminary nucleation may occur. The second region is the agitator pad area. In this area, the energy consumption rate is relatively high, so more secondary nucleation may occur. The final region is the main flow area. Therefore, in the heterogeneous nucleation system, which was often in the feed area because of the high local supersaturation concentration, a large number of nuclei formed. The higher agitation rate can reduce the initial local environmental concentration, and thus reduced the nucleation rate, which greatly improved the coating effect of the fly ash. This in turn improved the whiteness of the modified fly ash. When the calcium hydroxide concentration in the reactants was low, the growth of calcium carbonate crystals was affected, and the crystal growth was not sufficient. Therefore, the concentration of calcium hydroxide needs to be carefully chosen.

CONCLUSIONS

1. To improve the fly ash whiteness, the fly ash was modified by heterogeneous nucleation of calcium carbonate on the fly ash surface. When the calcium hydroxide concentration was 7% and the stirring speed was 500 rpm, most of the prepared calcium carbonate crystals were nucleated and crystallized on the surface of the fly ash. The coating effect of the fly ash was better and the whiteness improved, which reached a maximum of 59.70 ISO.
2. The use of crystal nucleation, growth microscopic processes, and the LaMer model theory changed the local supersaturation, increased the stirring speed, and increased the concentration of supersaturated solution required for subsequent calcium carbonate crystal growth by properly increasing the calcium hydroxide concentration. The better coating of calcium carbonate crystals on the fly ash surface provided a theoretical basis for analysis.

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