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BENCH-SCALE INVESTIGATION OF LIMESTONE SIZE EVOLUTION IN A FLUIDIZED BED COMBUSTOR

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ABSTRACT

The influence of temperature, heating rate and chemical reaction on fragmentation and attrition of limestone in a fluidized bed (FB) was investigated. The intensity of fragmentation and attrition was measured in the same apparatus but at different fluidizing velocities and fluidizing media. It was found that the heating rate has a positive effect on fragmentation for the tested limestones. The effect of bed temperature on limestone fragmentation was inconclusive. The influence of chemical reaction on the fragmentation seems to be complicated; CO₂ release due to calcination would prompt fragmentation while the sulfation would increase the gas diffusion resistance and depresses the fragmentation intensity. On the other hand, the CaSO₃/CaSO₄ layer was found to be attrition-resistant leading to small attrition rates. Attrition rate constant showed to decay exponentially with time and approaching a constant for all limestone particles. Particle sizes between 200-400μm have larger attrition rate constant than coarse ones perhaps due to their large specific surface area.

INTRODUCTION

Limestone is commonly used as a desulfurization sorbent in fluidized bed and circulating fluidized bed (CFB) boilers to reduce SO₂ emissions. After limestone is added to the furnace, substantial changes in the sorbent particle size distribution, namely comminution, can be caused by limestone fragmentation and attrition [1-7]. Based on previous studies, fragmentation is often classified into primary and secondary steps [6]. The primary fragmentation refers to the generation of fragments, either coarse or fine, immediately after the injection of limestone particles into the hot furnace [4, 6, 8, 9]. This process often occurs in the dense bed or in the splashing zone of either FB or CFB combustors. The secondary fragmentation refers to the generation of fragments mostly from high-velocity collisions against bed material or reactor walls and internals. Attrition refers to the generation of fine particles by abrasion and depends upon the resistance of the bed particles to surface wear. Size evolution caused by fragmentation and attrition is strongly coupled with the calcinations and sulfation processes as well as the overall mass balance in the CFB system. Thus, factors impacting fragmentation and attrition play important roles in the boiler performance.

Previous studies have investigated the impact of limestone type and size [2,4,7,10-13], fluidizing gas velocity [6,8,9] and temperature [7,14] on fragmentation. For a CFB boiler, scholars also found that fragmentation is influenced by the solids circulation rate [2,3,8] and by the inventory of inert bed material [13-14], etc. However, an investigation on the effect of chemical reaction, especially sulfation, on

limestone fragmentation is an issue of practical significance. In addition, the impact of particle size, temperature and heating rate on fragmentation remains a controversial topic in the literature [7,14]. Therefore, the aim of this work was to conduct a systematic study of limestone fragmentation and attrition in the FB reactor in order to further explore some of these factors.

A set of experiments on the primary fragmentation and attrition of two different limestones was conducted in this study. The effects of heating rate, temperature and initial particle size of the limestone were studied. Different fluidizing media (air, SO₂, CO₂) were used in the experiment to study the influence of calcination and sulfation on fragmentation and attrition behavior. The jet effect near the distributor was not studied.

EXPERIMENTAL

The bench-scaled fluidized bed reactor used in this study was described in detail previously [15]. The reactor was a round tube made of silica glass, with an inner diameter of 54 mm and height of 800 mm. The reactor was electrically heated and the main section could be maintained at a desired temperature with a deviation of $\pm 5^{\circ}\text{C}$. An air distributor (a porous plate type) was placed near the middle of the reactor. The section below the distributor was used to preheat the fluidizing gases. During the fragmentation experiments, inert bed material, *i.e.*, quartz sand (90-125 μm) was pre-laid on the air distributor. The limestone was then added in batch mode (20 g), with a particular initial size cut, and mixed with the quartz sand. The initial static height of the bed material was kept at about 40 mm for all tests.

A rather low, superficial gas velocity, U_g , was set for the tests at about 0.1-0.2 m/s, at a reactor temperature of 850°C, to minimize the attrition and secondary fragmentation. Thus, all of the fragments formed could be attributed to the primary fragmentation. After the limestone was added into the reactor for a prescribed time interval, all of the materials, including limestone fragments and bed material, were aspirated out and collected by a solids collection system. The bed material was then separated from the collected mixture by a sieve shaker, and the particle size distribution (PSD) of the residual fragments was obtained by sieving and weighing. The mass of the fragments in the size range of the inert bed material (90-125 μm) was estimated by measuring the weight loss during calcination in a muffle furnace.

As in a previous study [16], the coefficient of average particle size variation, F_d , was used to characterize the degree of particle size change, which can be expressed as $F_d = d_f/d_o$, where d_f is the average Sauter diameter of new PSD and d_o is the average Sauter diameter of the particles in the original sample. For purposes of discussion, another parameter called the fragmentation intensity coefficient (FIC), defined as $\text{FIC} = 1 - F_d$, was introduced to describe the intensity of fragmentation. The FIC can vary between zero (no change in particle size) and near unity (denoting a substantial decrease in particle size).

To measure the attrition rate by abrasion, a relatively high U_g (*e.g.*, $U_g \approx 0.5$ m/s) was used such that fines with a diameter less than 80 μm , generated by attrition, could be elutriated and then collected by the solids collection system. Before the adding of the testing sample, a certain amount of bed material of quartz sand (~ 160 g, 250-300 μm) was pre-loaded in the reactor. The quartz sand was abrasion resistant and

remained in the reactor under the selected U_g . The bed was put into operation with a preset U_g and bed temperature for a prescribed period until it was steady. The testing sample, with a mass of 50 g, was then added to the bed. At 10 minute intervals, the attrition rate, R_s , was obtained [1] by weighing the fine particles collected in the cyclone with a total sampling time of about one minute duration. From these data, the attrition rate constant, K_a , was calculated. The experiment was continued until the attrition rate became steady. In this study, the influence of chemical reaction was also evaluated by changing the fluidizing media. Limestone was first calcined in the FB for 10 minutes under an air atmosphere; and then different mixtures of CO_2 and SO_2 were subsequently used to study the influence of sulfation.

Two kinds of limestone (types A and B) were studied. The $CaCO_3$ and $MgCO_3$ compositions measured by x-ray diffraction are listed in Table 1. Each limestone was classified into 3 size groups of 200-400 μm , 400-600 μm , and 600-800 μm in order to study the effects of the initial particle size.

Table 1. The composition of the limestone samples (% in mass)

Sample	Ca	Mg	$CaCO_3$	$MgCO_3$	Other
A	39.4048	-	98.51	-	1.49
B	38.5512	0.7811	96.38	2.73	0.89

RESULTS AND DISCUSSION

Effect of Limestone Type and Original Size

Figure 1 shows the FIC of both limestone types at a temperature of 850°C under an air atmosphere in the FB furnace. A higher FIC value represents a higher fragmentation intensity and a smaller average particle size produced. For both limestone types, the enhanced fragmentation of the tests with a larger initial particle size classification is apparent. However, a previous experimental study [15] indicates that the effect of particle size on fragmentation is not always the same, and depends on the limestone type. The micro-structure of the particles could be very different for different limestone samples and could cause significant differences in fragmentation and attrition [8]. In this study, it is believed that the impact of the particle micro-structure, combined with other effects such as heating rate, could be the reason for the ambiguous effect of initial particle size. This phenomenon should be studied in more detail in future research.

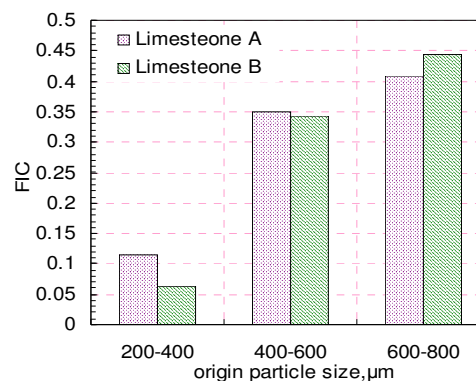


Figure 1. Fragmentation intensity coefficient (FIC) of limestones A and B under air atmosphere in FB (850 °C)

Effect of Temperature on Fragmentation

In order to study the influence of temperature on the fragmentation of limestone, a test was conducted under different temperatures (850 and 900°C) in the FB reactor. Figure 2 and Figure 3 show the changes in the cumulative particle size distributions of limestone A with different initial sizes. The data appears to indicate, albeit not conclusively, that the average particle size d_s increases with temperature except

sizes between 400-500 μm . Other study [14] showed that high temperature enhances the attrition of particles but lessens the primary fragmentation. The author explained that enhancement of CO_2 release at high temperature is not strong enough to prompt increased fragmentation in the bed. More studies are necessary in the future.

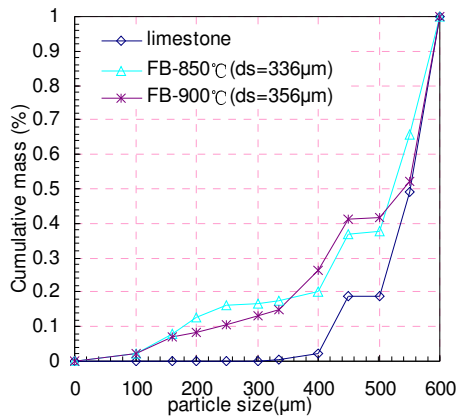


Figure 2. Effect of temperature on the PSD of fragmentation product (A, 400-600 μm)

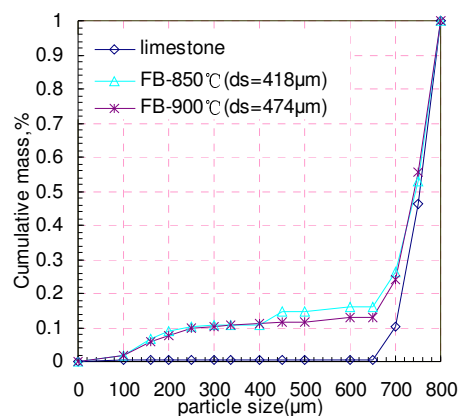


Figure 3. Effect of temperature on the PSD of fragmentation product (A, 600-800 μm)

Effect of Heating Rate on Primary Fragmentation

In order to simulate the effect of heating rate on the primary fragmentation of limestone, various experimental conditions were used. In Figures 4 and 5, FB refers to the baseline operational condition, C refers to the calcination of limestone in the reactor without inert bed material (silica sand), and FB-H refers to the introduction of a higher limestone weight (50g) to decrease the heating rate in the FB.

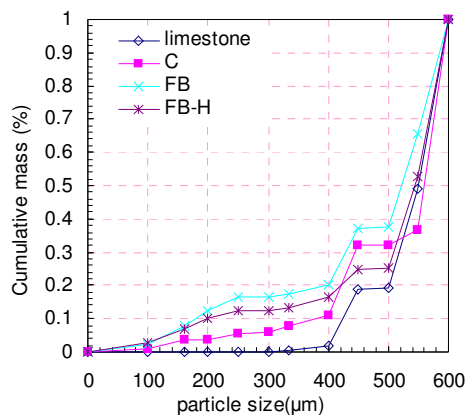


Figure 4 Effect of heating rate on the PSD of fragmentation product (A, 400-600 μm)

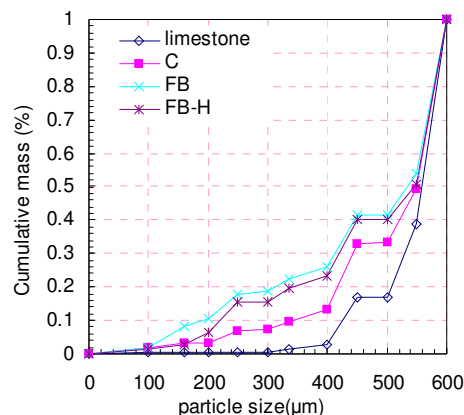


Figure 5 Effect of heating rate on the PSD of fragmentation product (B, 400-600 μm)

As shown in Figures 4 and 5, compared with the initial limestone particle size, lime calcined under FB condition is much finer than that of lime PSD obtained under the 'C' experimental condition. Under the 'C' experimental condition, where no inert bed material was used, the thermal heating rate was mainly caused by radiation from the wall and convection of high temperature gas, which induced a smaller heating rate than that provided by silica sand bed. Therefore, the heating rate could enhance the fragmentation of the limestone, especially for limestone B. The relative contribution of the higher heating rate on fragmentation, provided by the silica sand particles, is difficult to quantify, because it is coupled with the mixing-induced attrition caused by

the purely mechanical stresses of the sand particles on the limestone.

The comparison between the PSDs from the FB and FB-H conditions also illustrates the promotion of thermo-mechanical and chemical effects by the heating rate on the primary fragmentation intensity. Limestone is calcined into lime in the furnace (endothermic process) and at the same time experiences thermal stresses as it is heated up. The time required for complete fragmentation is about 4 to 6 minutes longer for the larger sample weight (FB-H). But the effect of such a small difference on attrition and particle size evolution is probably negligible. Because the output of the electrical furnace is constant, less limestone sample means a higher heating rate. In general, an improved heating rate can enhance calcination and prompt primary fragmentation. Therefore, as shown in Figures 4 and 5, the fragmentation product size of FB-H is less than that of FB condition.

Effect of Fluidizing Media on Fragmentation

The product gas from industrial CFB boilers is composed of CO_2 , SO_2 , NO_x , etc. These gas species may have a great impact on limestone fragmentation in the boilers. Previous studies have found that the existence of a high CO_2 concentration will suppress the calcination and fragmentation of limestone [9,15,16]. SO_2 calcined lime absorbs SO_2 to form $\text{CaSO}_3/\text{CaSO}_4$, which may also suppress fragmentation.

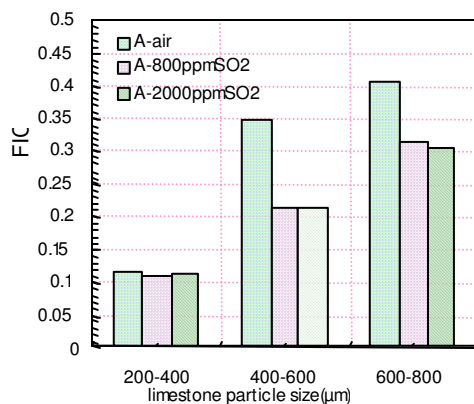


Figure 6 Fragmentation intensity of limestone A with SO_2 atmosphere

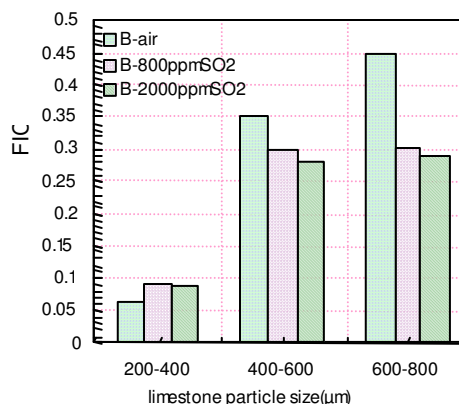


Figure 7 Fragmentation intensity of limestone B with SO_2 atmosphere

Figures 6 and 7 show FIC values of two kinds of limestone under different atmospheres at a reactor temperature (850°C). It's obvious that the SO_2 suppressed the fragmentation of both kinds of limestone under the conditions used in this study, at least for the larger particle sizes

Both limestone types have the largest fragmentation intensity under an air atmosphere. The possible reason may be that fresh lime on the surface of the particle reacted with SO_2 and produced a harder, attrition-resistant layer of $\text{CaSO}_3/\text{CaSO}_4$ product over the particle surface and may hinder the CO_2 release. Figure 8a shows CO_2 concentration variation during the fragmentation process under different fluidizing media. The release of CO_2 is faster with air initially as comparing to the SO_2 atmosphere. But with the uncertainty of reading in low value the trend seems reversed later. Figure 8b shows the accumulated CO_2 released (normalizing to 100%). As shown for the same percent of calcinations completed, fluidizing media with air requires less time than that with SO_2 case. This seems to confirm the

suppressing effect of the SO₂ on CO₂ release. On the other hand, the variation of SO₂ concentration has no obvious impact on the FIC of limestone with short time duration. The sulfation reaction of CaO and SO₂, as a relatively long duration process, will take hours to complete. Therefore, during the short time of primary fragmentation, the variation of SO₂ concentration from 800 ppm to 2000 ppm may have no appreciable effect on the thickness of the layer and subsequently on the FIC.

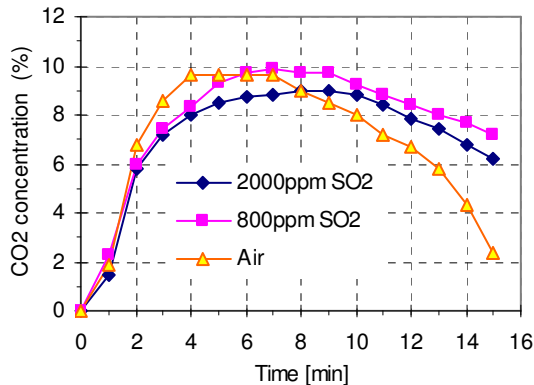


Figure 8a CO₂ concentration variation during fragmentation process (A, 400-600mm)

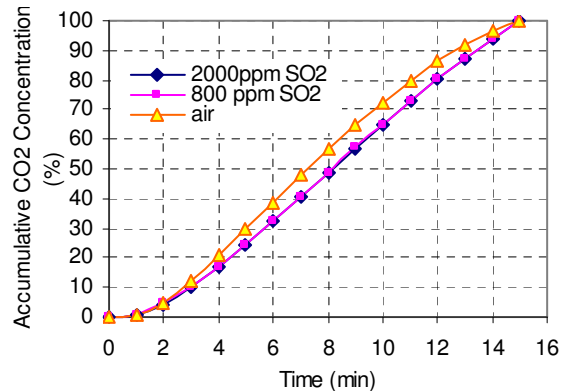


Figure 8b Normalized CO₂ concentration accumulated during fragmentation process (A, 400-600mm)

Generally, three mechanisms are attributed to the limestone fragmentation: thermal stress at high temperature, high internal pressure caused by organics or water evaporation and the CO₂ release during calcination [5]. Calcination is a chemical reaction process that will produce CO₂ and lime (CaO). At a certain temperature, calcination reaction occurs only if the partial pressure of CO₂ in the environment is lower than the CO₂ pressure at chemical equilibrium [9,18]. The existence of high CO₂ concentration in the environment will suppress the calcination reaction [16]. As shown in Figure 9, fragmentation was suppressed under an atmosphere of 15% CO₂+2000 ppm SO₂, as evidenced by the fact that the size change of limestone was insignificant. The results further confirmed the contribution of the calcination reaction to the fragmentation of limestone.

Effect of the Sulfation on Attrition of Limestone

The degree of (secondary) fragmentation that can be attributed to sulphation processes other than calcinations and rapid gas release is trivial. Thus, comminution of lime and its sulphate products is mainly attributed to attrition by abrasion [6]. Attrition by abrasion generates fine particles that are quickly elutriated by the high fluidizing gas velocity and collected by the cyclone at the outlet of furnace. The average size of the product remaining in the

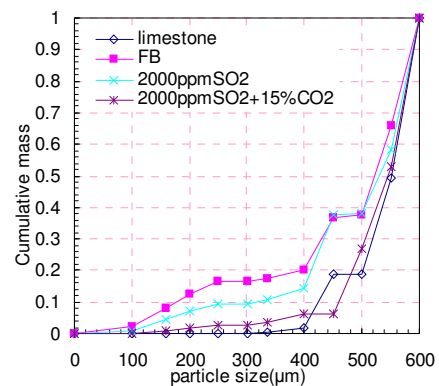


Figure 9 PSD of fragmentation product (A, 400-600 μm)

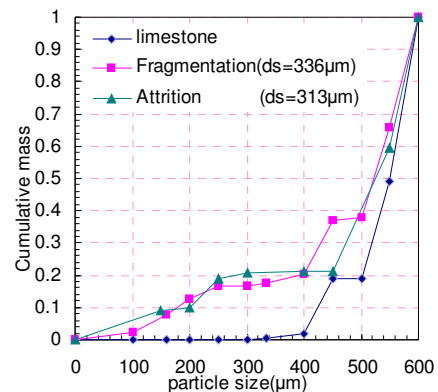


Figure 10. PSD comparisons of attrition and fragmentation product (A, 400-600μm)

reactor after the attrition process is finer than with the primary fragmentation product, except for particle 450 μm as shown in Figure 10. In this study, the attrition process lasted for about 150 minutes at a temperature of 850°C and a fluidizing velocity of 0.5 m/s in the FB reactor.

Figure 11 shows the change of K_a for limestone A with three initial particle sizes. K_a is found to decay exponentially with time, and then approaches a constant (K_∞). Regardless of the initial value of K_a for limestone, finer limestone samples less than 400 μm eventually have a higher K_∞ . The attrition rate constant of K_∞ for particles larger than 400 μm shows small difference. Finer particles have a larger specific surface area for the same inventory and may experience more abrasion.

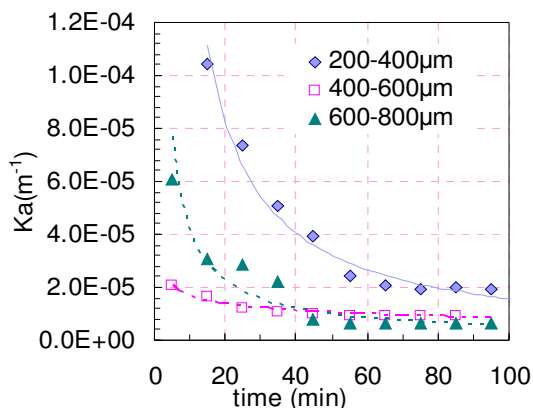


Figure 11. Change of attrition rate constant of limestone A (air atmosphere)

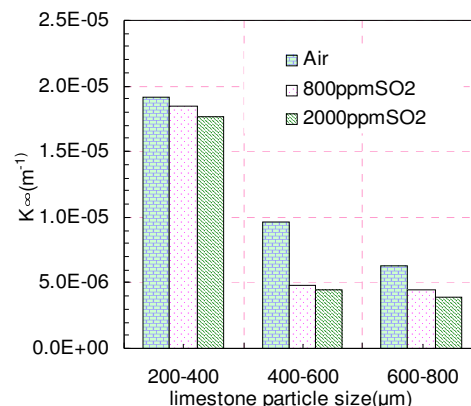


Figure 12. Attrition rate constant K_∞ of limestone A

The influence of sulfation on the attrition of limestone and its products was shown in Figure 12 for limestone sample A. After the limestone was calcined in the FB for ten minutes under an air atmosphere, the fluidizing gas was switched to a mixture of air and SO_2 . The attrition rate of the sample under an SO_2 atmosphere was found to exhibit a trend that was similar to that under an air atmosphere in size effect up to a factor of 2. Similar to other studies [6,8], the higher SO_2 concentration produces lower K_∞ due to more attrition resistant.

CONCLUSION

Two limestone samples were selected and tested in a bench-scale bubbling fluidized bed reactor under various conditions to study the limestone fragmentation and attrition. Experimental results confirmed that fragmentation and attrition could be significantly affected by limestone type, initial size, heating rate, fluidizing media, and temperature. The average size of the particles decreased during the fragmentation process. The heating rate and mechanical collision in the FB have been found to enhance the fragmentation, while the temperature seems to have negative effect on fragmentation. Sulfation reactions suppress the fragmentation of limestone due to the gas diffusion resistance of the $\text{CaSO}_3/\text{CaSO}_4$ layer. The layer of $\text{CaSO}_3/\text{CaSO}_4$ surface is attrition resistant. The sulfation reaction leads to a smaller attrition rate of limestone products under an SO_2 atmosphere than under an air atmosphere.

ACKNOWLEDGEMENT

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NOTATION

U_g	gas superficial velocity in tube, ms^{-1}	R_a	attrition rate, kgs^{-1}
K_a	attrition rate constant, m^{-1}	K_∞	final attrition rate constant, m^{-1}
d_o	average Sauter mean diameter of the original PSD, μm		
d_f	average Sauter mean diameter of the new PSD, μm		

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