Note

Carbonation Reaction of CaO in Jet Milling of CO₂ Gas

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1. Introduction

Due to the increased concerns with environment and energy issues, the industrial activities have been regulated in many areas. In particular, global warming by greenhouse gas such as CO₂ produced from steel production plants is becoming serious. To meet the demands of those issues, many efforts have been made to decrease CO₂ emission from steel industries.

The slags generated in ironmaking and steelmaking processes contain a high fraction of CaO that exothermically reacts with CO₂ to form carbonate. This carbonation reaction makes slags an attractive source for CO₂ sequestration. It is called “mineral CO₂ sequestration process” and a variety of attentions have been paid to this process^{1–5)} due to its high CO₂ storage potential and stability of final product. There are two approaches to mineral CO₂ sequestration, which are (1) direct carbonation which binds the solid-state mineral with gaseous CO₂, and (2) aqueous processes which extract calcium ions from the minerals into solution, followed by precipitation of either the carbonate or an intermediate product which is carbonated in a separate step. Despite of slow reaction rate and complexity of the process, previous researchers have focused on the aqueous process which is based on water–solid–gas reactor because the process can react at much lower temperatures than that of direct carbonation.

The advantage of direct carbonation is its inherent simplicity compared with aqueous process. The exothermic nature of the CaO carbonation reaction also gives a chance to utilize generated heat in the case of direct carbonation. The main constraint for cost effective implementation of direct carbonation lies in the slow rate of the carbonation reaction. It is well known^{6,7)} that the carbonation reaction of CaO is divided into two stage; chemical reaction-controlled stage which shows fast conversion followed by sudden transition to a much slower stage controlled by diffusion through the CaCO₃ product layer. In this sense, it is of great importance to have fast whole carbonation reaction rate by direct carbonation, resulting in the successful implementation of economically attractive process of mineral CO₂ sequestration. Therefore, the jet milling of CaO particles with CO₂ gas has been carried out to find out the feasibility of “reactive comminution” in the present study.

2. Technical Background—Jet Milling Process (Reactive Comminution)

The CaO carbonation reaction of industrial scale requires

fine powder of CaO-containing mineral or slag, which provides sufficient surface area for rapid conversion to CaCO₃. It is generally recognized that the comminution or grinding process is so energy intensive that the energy required to grind the minerals or slags should not exceed the CO₂ sequestration benefit.⁴⁾ Jet mills are widely used in industries for grinding solid materials although they are still high energy consumers. However, in the present study, a jet mill has been applied not only to obtain fine powder, but also to carry out the CaO carbonation reaction and to remove CaCO₃ product layer covering CaO core simultaneously. Due to these two extra benefits, the energy consumption in grinding process might be compensated for. The atmosphere of a jet mill process is easily controlled by introducing any particular gas, *e.g.* CO₂ gas can be used for jet milling instead of air. The grinding is achieved by high-velocity collisions among particles. The fresh breakage surface is believed to be very reactive. It is also expected that the local temperature at the surface of collided particles must be higher than ambient temperature due to the impact energy. Thus, if the grinding of CaO particles is carried out in CO₂ atmosphere, the carbonation reaction at the breakage surface may occur during the grinding process without any external heating. As already mentioned, CaCO₃ product layer on the CaO core retards the carbonation reaction. If formed CaCO₃ is effectively removed and the fresh surface can be exposed during jet milling process, the carbonation reaction can nearly come to full completion. It is another expected benefit for using the jet milling. The grinding process combined with reaction is named “reactive comminution” process.

3. Experimental

3.1. Apparatus

A jet mill of lab scale spiral type was employed for dry carbonation as shown in Fig. 1. The diameter and height of the grinding chamber is 155 and 20 mm, respectively. The nozzle diameters for materials feeding and product output are 5 and 20 mm, respectively. Six nozzles of gas feeding in grinding chamber are positioned inward with 26° of angle with respect to the tangent of the chamber side surface. All the above conditions were fixed during experiment because those parameters control grinding efficiency.^{8,9)} Materials were fed into the grinding chamber through the material feeding nozzle and were accelerated by the compressed gas injection. Developed high-speed rotational flow induced the collisions among particles or between particle and inner lining of the chamber, resulting in creating ultra fine particles. Centrifugal force holds larger particles in the grinding space while centripetal force drives fine particles toward the center for discharge port to classifier chamber.

Fig. 1. Schematic view of a jet mill.

3.2. Materials

High purity of CaO powder for each experiment was freshly prepared by decomposing the CaCO₃ powder of 99.9% purity in a box furnace of air atmosphere. Each CaCO₃ powder was heated to 1 273 K and held for 2 h at the temperature for the completion of CaCO₃ decomposition, and thereafter cooled to room temperature. Then, it was directly subjected to the jet milling experiments to minimize the effect of H₂O absorption.

3.3. Procedure

The reactive comminution was carried out by using air, 100% CO₂ and 80%N₂–20%CO₂ gas mixtures at room temperature. The injection gas pressure was fixed to be 4 atm. The gas pressures for grinding and feeding in the jet mill were fixed at 0.1 MPa and 0.3 MPa, respectively. The jet milling of sample took 10 min. The CaO feeding rate was changed from 3.0 to 60.0 g/min.

3.4. Analysis

Initially the particle size before and after jet milling was measured by using the laser diffraction particle measurement system. However, the measurement was not successful due to the strong agglomeration tendency of CaO particles. Thus, the average size was estimated based on the SEM images of particles. After the reactive comminution, about 25 mg of ground CaO powder was charged into an Al₂O₃ crucible (ID: 5 mm) and set in a thermogravimetric analysis (TGA) system. Then the sample in the TGA system was heated at the heating rate of 10 K/min up to 473 K to remove the effect of H₂O and again heated up to 1 273 K in de-hydrated and de-oxidized Ar atmosphere. The temperature and the sample's weight change were continuously recorded. The sample was held at 1 273 K about 1 h to confirm the complete dissociation reaction of CaCO₃. After that, the sample was naturally cooled down. The CaCO₃ formation during the reactive comminution process was calculated by the decrease of the sample weight because the sample's weight decrease is solely due to the decomposition of CaCO₃. X-Ray diffraction analysis was also done to verify the CaCO₃ formation.

4. Results and Discussion

4.1. Particle Size Distribution

The samples before and after the reactive comminution are shown in Figs. 2(a), 2(b) and 2(c), respectively. The initial CaO sample is composed of several CaO blocks combined together and forms large aggregates of about 30–40 μm. After grinding work, initial CaO aggregates were separated into smaller blocks which show irregular size distribution. However, some of the aggregates are remaining as large blocks. Numerous fine particles less than 5 μm were also observed. It is clearly shown that the surface morphology before and after the milling is quite different.

4.2. Estimation of Reacting Time

In general, the residence time is defined as the average time that a substance spends in a processing vessel. The mean residence time (t_m) of a material of any size R_i is given by Eq. (1).

$$t_m = t_m(R_i) = \frac{W}{F} \dots\dots\dots(1)$$

Fig. 2. SEM micrographs of (a) initial CaO particles before jet milling and (b) carbonated particles after jet milling in 80%N₂–20%CO₂ gas atmosphere (c) lower magnification.

Fig. 3. The relation between the residence time and the feeding rate in 100% CO₂ atmosphere.

where W is the weight of the solids inside the chamber and F is the feed rate of the solids.

The mass hold-up in the mill chamber was measured by manually collecting the materials by careful brushing and then its weight was measured. Gas composition was fixed to 100% CO₂ in the experiments estimating residence time. The evaluated residence time as a function of feeding rate is shown in Fig. 3. The residence time depended on the feeding rate. The maximum residence time was 3.5 s at the feeding rate of 6.7 g/min. From this result, the average reacting time of carbonation reaction during jet milling must be within 3.5 s.

4.3. Reaction Extent

CaO can easily absorb H₂O and forms Ca(OH)₂. If CaO absorbs H₂O during the reactive comminution, the weight change is affected by not only CaCO₃ formation but also

Fig. 4. Thermogravimetric curve for the CaO particles after jet milling in 100% CO₂ atmosphere.

Fig. 5. SEM micrograph of CaO particles after jet milling in 100% CO₂ atmosphere at large magnification.

Fig. 6. Variation of carbonation conversion with treatment time in 85%Ar-15%CO₂ at 773 K, 873 K and 973 K.

Ca(OH)₂ formation. To examine the effect of Ca(OH)₂ formation during the jet milling, the decompositions of Ca(OH)₂ and CaCO₃ were analyzed by using TGA system. It was confirmed that Ca(OH)₂ decomposition starts from around 473 K and finishes at around 773 K.

The typical results of TGA curve for jet milling CaO particles with CO₂ gas injection is shown in Fig. 4. The weight loss is found to start from about 973 K. This weight loss is fully due to the CaCO₃ decomposition, since the weight loss is started from about 973 K. In the case of using air for jet milling, the weight loss of ground CaO powder was not observed.

The sample surface after the reactive comminution in large magnification was shown in Fig. 5. As shown in Fig. 2(a), the initial CaO is composed of peanut-like fine units with diameter of about 1.0 μm. The sample after the grinding has quite different appearance. Significant portions of the previously existed pores between peanut-like elements were filled and the flat surface was observed.

To investigate the reaction behavior in the reactive comminution, the carbonation reaction rate of CaO powder with 85%Ar-15%CO₂ at 773 K, 873 K and 973 K were measured by using thermogravimetric method. The reaction conversions as a function of time are shown in Fig. 6. It shows the typical CaO carbonation behavior.^{6,7)} Namely, the reaction occurs rapidly by the surface chemical reaction at the initial stage. Following this, the rate decreases due to the diffusion limitation through the produced dense CaCO₃ layer. The appearance of quenched sample after 5 min carbonation was shown in Fig. 7. It is clear that the particle surfaces are fully covered with CaCO₃. It shows the almost same appearance shown in Fig. 5. These similar appearances between them clearly indicate that the carbonation reaction of CaO occurs during the reactive comminution process. The existence of CaCO₃ was also confirmed by X-ray diffraction analysis.

Depending on the experimental conditions, the average conversion fraction of charged CaO particles was varied from 5 to 10%. However, no clear relationship between the conversion and experimental parameters was found. In a particular case, the conversion of 20% was achieved. However, the reproducibility is quite poor. From the residence time evaluation, the conversion of 10% can be accomplished at most within 3.5 s. The average conversion rate of 2.8%/s in CO₂ jet milling process is quite fast compared with that of 0.1%/s in the ordinal carbonation reaction shown in Fig. 6. Practically, much faster conversion rates can be expected by optimizing the comminution parameters such as feeding rate, initial particle size, gas injecting rate and total pressure. The low conversion of 10% due to the short residence time in the present study can be easily

Fig. 7. SEM micrograph of CaO particles after carbonation treatment in 85%Ar-15%CO₂ furnace for 5 min at 773 K.

enhanced by the combination of several jet milling steps. Therefore, the reactive comminution process can be considered to be one of the effective and practical CaO carbonation processes if the experimental parameters were fully optimized in future investigation.

5. Conclusions

The carbonation reaction of CaO by reactive comminution process was investigated. In the present conditions, the following conclusions were obtained:

- (1) The carbonation reaction of CaO occurred during CO₂ gas jet milling process even at room temperature.
- (2) The average conversion of CaO to CaCO₃ was found to be about 10% with the reaction time of at most 3.5 s.
- (3) The reactive comminution process can be one of the promising methods for effective CO₂ sequestration.

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