Effects of Particle Size Distribution on Limestone Dissolution in Wet FGD Process Applications

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The kinetics of limestone dissolution in the wet type flue gas desulfurization (FGD) processes has been studied. The rates of dissolution and particle size reduction were measured in both batch and continuous reaction systems for limestone of different size distribution. A predictive model was developed based on mass transfer mechanism. It was in good agreement with experimental data. Moreover, the rate of dissolution for 25 limestones of different composition and size distribution were measured in apparatus with a sulfur dioxide absorber which simulated FGD processes. The model was also in good agreement with these results.

INTRODUCTION

The mainstay of flue gas desulfurization (FGD) processes for thermal power plants with the object of environmental protection has been the wet type limestone scrubbing process. In this process, limestone dissolves into absorbent slurry and neutralizes sulfur dioxide, so the dissolution rate of limestone is one of the most essential kinetics in FGD processes; therefore, accurately evaluating the dissolution of limestone is important for not only designing of a FGD process but also operation of the plant [9].

Many studies on limestone dissolution have been carried out so far. Morse and Plummer et al. discussed the basic kinetics of dissolution [7, 9]. Generally, the limestone dissolution is considerably affected by the pH value of liquid and the particle size of limestone. The correlation between the pH value and limestone dissolution rate was studied by Chan et al. and Ellis [2, 5], and research regarding the particle size was studied by Tress et al. [11]. Compton et al. carried out experiments on the morphology of the limestone dissolution [3, 4]. Furthermore, the model being able to predict limestone reactivity as well as FGD performance was developed by Gage et al. [6]. Few previous studies, however, have discussed the variation of the particle size distribution during dissolution, although the particle size is one of the most significant factors in dissolution.

In this study, the variation of the particle size distributions of limestone through the dissolution reaction were measured both in the batch and continuous type test apparatus. The obtained data were compared with the results which were expected by the mathematical model. Furthermore, the dissolution rates of limestone having various particle size distributions and compositions were measured, using wetted-wall column equipment which simulated the absorber of wet FGD process.

MODEL DESCRIPTION

In the vicinity of pH 5, the dissolution of limestone in solution is supposed to be the reaction between the limestone and hydrogen ions and is expressed as follows:

\[ \text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \]  

(1)
On the dissolution equation 1, Toprac et al. proposed dissolution rate equations by combining the rate in a stagnant fluid and an agitated fluid as mentioned below [10]. When the limestone particles are assumed to be spherical, the dissolution rate can be expressed by equation 2, and the mass transfer coefficient in the stagnant fluid is given by:

\[
\frac{dV_e}{dt} = -\frac{\pi d^2 k_L \Delta C}{P_m} \tag{2}
\]

\[
Sh = \frac{k_L \cdot d_p}{D} = 2 \tag{3}
\]

From equation 2 and 3:

\[
\frac{dV_e}{dt} = -\frac{\pi \Delta C}{P_m} 2Dd_p \tag{4}
\]

The correlation equation of the mass transfer coefficient in the agitated fluid was studied by Calderbank et al. [1] who presented as:

\[
k_L \cdot S_c^{2/3} = 0.13 \left( \frac{\epsilon \cdot \rho_e}{\rho_c} \right)^{1/4} \tag{5}
\]

\[
S_c = \frac{\nu_c}{D} \tag{6}
\]

From equation (2), (5) and (6), the dissolution rate in the agitated fluid is given by:

\[
\frac{dV_e}{dt} = -\frac{\pi \Delta C}{P_m} 0.13 \left( \frac{\epsilon \cdot \rho_e}{\rho_c} \right)^{1/4} \left( \frac{\nu_c}{D} \right)^{-2/3} d_p^{2/3} \tag{7}
\]

When equation (4) and (7) are combined, the dissolution rate is obtained as follows:

\[
\frac{dV_e}{dt} = -\frac{\pi \Delta C}{P_m} \left[ 2Dd_p + 0.13 \left( \frac{\epsilon \cdot \rho_e}{\rho_c} \right)^{1/4} \frac{\nu_c}{D} \right] d_p^{-2/3} \tag{8}
\]

Equation 8 can be rewritten as:

\[
\frac{dV_e}{dt} = -k_c V_p^{1/3} - k_B V_p^{1/3} \tag{9}
\]

Where

\[
k_c = \frac{3.63D \Delta C}{P_m} \left( \frac{0.08065}{D} \right)^{1/4} \left( \frac{\nu_c}{D} \right)^{-2/3} \tag{10}
\]

Equation 9 can be solved analytically. When the fraction of unreacted limestone is used instead of volume of particle as:

\[
t = \frac{3}{k_c B} \left( \ln \left( \frac{1 + B V_{p}^{1/3} f_j^{1/3}}{1 + B V_{p}^{1/3}} \right) + B V_{p}^{1/3} (1 - f_j^{1/3}) \right) \tag{11}
\]

This equation shows a fraction of dissolution of limestone having a same particle size in the batch reaction system. Usually, the limestone used in the FGD process has broad particle size distribution. Therefore, equation 10 should be solved per each particle size, and the fraction of dissolution of limestone with a particle size distribution the batch reaction system is expressed by:

\[
F_B = \sum_{j=1}^{n} \left( \phi_j \frac{1}{t} \int_{0}^{\infty} f_j \cdot \exp \left( -\frac{t}{\tau} \right) \, dt \right) = 1 - \eta_B \tag{11}
\]

Meanwhile, the reaction of limestone in most of the FGD process happens to a continuous reaction system, so the consideration on the residence time distribution of CSTR for the limestone particles should be required. Eventually, the fraction of dissolution in the continuous reaction system is given by:

\[
F_c = \sum_{j=1}^{n} \left[ \phi_j \frac{1}{\tau} \int_{0}^{\infty} f_j \cdot \exp \left( -\frac{t}{\tau} \right) \, dt \right] = 1 - \eta_c \tag{12}
\]

As is clear from its definition, \(k_c\) in equation 10 is proportional to a difference in the concentration which is the driving force when the diffusion coefficient and molar density of limestone are constant. At the pH value prevailing in the absorber of FGD process, this difference in concentration can be considered to be hydrogen ion concentration. If the activity coefficient of the hydrogen ion is presumed to be constant, \(k_c\) is further defined by:

\[
k_c = k_a \cdot 10^{-\phi_H} \tag{13}
\]

**EXPERIMENT**

**Apparatus**

Figure 1 shows batch type test apparatus. Two reactors which had different volume were prepared. One reactor, a volume of 21, was used to obtain the data regarding the fraction of dissolution vs. the particle size distribution. The other reactor, a volume of 0.21, was used to obtain the data regarding the time vs. the fraction of dissolution. The liquid in the reactor was kept at a constant temperature through the jacket. During all the tests, the constant pH was kept by means of adding acid with pH controller. The particle size distribution of unreacted limestone was measured by standard sieves for over 20 μm and photo extinction apparatus for under 20 μm. The test conditions were as follows: Reactor volume-21 (0.21); limestone concentration—45g/900 ml (0.5g/lOOml); acid solution—6N-HCl (1N-HCl); liquid pH—5.0; and temperature—50°C. The values in the parenthesis show the test conditions for the time vs. the fraction of dissolution. The constant type test apparatus is shown in Figure 2. The reactor had a volume of 81 and was kept at a constant temperature in the same way as the batch type test apparatus. In this apparatus, an acid was quantitatively added (this corresponds to the absorbed amount of sulfur dioxide in the FGD process) and limestone was fed continuously to keep constant pH value. This apparatus can simulate feeding of limestone and discharging of gypsum in the absorber tank in FGD process. In
order to simulate the FGD process more accurately, it might be better to use sulfuric acid to be added, but hydrochloric acid was used in this tests to prevent formation of gypsum, because if gypsum particle was formed, it would be difficult to measure the particle size distribution of unreacted limestone. Using the continuous type test apparatus, data regarding the fraction of dissolution and particle size distribution of unreacted limestone were obtained. The particle size distribution was measured by the same way as the batch type test. The test condition were as follows; Hydrochloric acid load—100mmol/L h; liquid pH—4.8 to 5.5; and temperature—50°C.

The wetted-wall column apparatus is shown in Figure 3. The wetted-wall column can simulate the practical absorber in an actual FGD process. Table 1 summarizes the specifications of the test apparatus and the operating conditions. Synthetic flue gas fed at the top of the wetted-wall column came in contact with a co-current flow of liquid film falling down the column wall. Air was sparged into the tank to oxidize dissolved sulfite completely. The dissolution rate of limestone was calculated from the amount of absorbed sulfur dioxide; however, the particle size distribution of unreacted limestone could not be measured in this test due to coexistence of gypsum particles.

Material

A limestone produced in Japan was used for testing with the batch and continuous type test. This limestone had the following composition: Purity of calcium carbonate—98.0 wt. %; MgO—0.4%; and acid insoluble—0.28 wt. %. Three limestone samples having different particle size distribution were prepared as follows:

1. Limestone, 95 wt. % of which passed through a 45 μm sieve and a mean diameter of 9.3 μm.
2. Limestone, 95 wt. % of which passed through a 75 μm sieve and a mean diameter of 10.5 μm.
3. Limestone, the particle size of which was adjusted from 20 μm to 45 μm by standard sieves.

For wetted-wall column test, 25 samples of limestone collected from various places of the world were prepared.

Results and Discussion

Figure 4 shows the relationship between the time and the fraction of dissolution in the batch test. In this figure, the limestone which reaches a higher fraction of dissolution in shorter reaction time has a higher reactivity. In the test, limestones with different particle sizes of the sample were used. The relation of the particle size distributions of the limestone was 45 μm 95% passing < 75 μm 95% passing < 20-45 μm. The measured values show higher reactivity in this order. The solid curves in the figure show the calculated values by equation 10 and 11, and they are in good agreement with the obtained data. The following values were used at the dissolution rate

![FIGURE 4. Dissolution rate of limestone in batch type test.](image-url)
constant and enhancement factor which were dissolution parameters.

\[ ka = 3.4 \times 10^{-9}, \ B = 200000 \]

The value of \( B \) is relatively higher than those (26000 to 88000 [l/m]) obtained by Toprac. The reason might be attributed to the difference of agitating conditions. The fact that the limestone of the same composition and from the same place but having different particle sizes can be expressed by the same dissolution parameters show that equations (10) and (11) allow accurate calculations of the effect of particle size. The particle size distribution of unreacted limestone in the batch type test was measured at several fractions of dissolution. Figure 5 shows the particle size distribution of the unreacted limestone. It indicates that as the dissolution progresses, the particle size of unreacted limestone shifts to the larger values. This can be simply explained by the fact that as: smaller particles have larger specific areas dissolve at a greater rate, and they disappear sooner than coarser one. The solid curves in Figure 5 give the values calculated by the dissolution rate equations like those in Figure 4. The measured values are in good agreement with the calculated values.

The fractions of dissolution measured and calculated at various pH values in the continuous reaction system are shown in Table 2. Figure 6 and 7 show the particle size distributions of unreacted limestone samples of 45 \( \mu \)m 95 wt. % passing and 75 \( \mu \)m 95 wt. % passing. The particle size distributions of unreacted limestones obtained in the continuous type test also shift to the larger values when the fraction of dissolution become greater, like in the batch type test, but the degree of shifting is smaller than in the batch system. For instance, for the sample of 45 \( \mu \)m 95 wt. % passing, the fraction of dissolution at which mean diameter of unreacted limestone becomes 18 \( \mu \)m is 95% in the continuous type test but 70% in the batch type test. It is considered that as fresh limestone of smaller particle size is constantly fed into the continuous reaction system, smaller particles are more likely to exist in it than in the batch reaction system. The calculated values in Table 2 and the solid curves in Figures 6 and 7 are values obtained by using equation (12). For the dissolution parameters, the same values as for the batch type test were used. In the continuous type test, the measured and calculated values are in good agreement, and they confirm that the dissolution rate equations in this study also holds good for the continuous type test and can be expressed by the same dissolution parameters. In addition, the results with the continuous type test show that the measured and calculated values at various pH values correspond well each other, and that equation 13 holds good in the pH range in this test.

The tests and analyses described above have shown that the dissolution rate equation in this study is applicable to the particular limestone produced in Japan. However, limestone used in a FGD process is usually produced from a mine near the plant, due to economical reasons, of which the characteristics may vary from quarry to quarry. Moreover, hydrochloric acid was used in the test as an acid to dissolve the limestone, but in an actual FGD plant, limestone reacts with an acid formed by absorption of sulfur dioxide. Therefore, 25 limestones were collected from various places of the world and were examined for their dissolution rates using the wetted-wall column apparatus which can simulate the absorption of sulfur dioxide. Figure 8 shows the relation between the dissolution rate constants and pH values of these limestones. In this test, the dissolution rate constants in the wetted-wall column and in the tank can be separately obtained through measuring the amount of absorbed sulfur dioxide in the wetted-wall column and pH values at both the bottom of the wetted-wall column and the tank. Therefore, the data shown in Figure 8 includes the rate constants obtained in both the wetted-wall column

![Figure 5](image1.png)

**FIGURE 5.** Particle size distribution of unreacted limestone in batch type test (particle size distribution of initial limestone; 45\( \mu \)m 95% passing).

![Figure 6](image2.png)

**FIGURE 6.** Particle size distribution of unreacted limestone in continuous type test (particle size distribution of initial limestone; 45\( \mu \)m 95% passing).

![Figure 7](image3.png)

**FIGURE 7.** Particle size distribution of unreacted limestone in continuous type test (particle size distribution of initial limestone; 75\( \mu \)m 95% passing).

### Table 2 Fractions of Dissolution Obtained by Experiment and Calculation

<table>
<thead>
<tr>
<th>Particle size of initial limestone</th>
<th>Liquid pH</th>
<th>Fractions of Dissolution ( – )</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>45( \mu )m 95% passing</td>
<td>5.5</td>
<td>0.895</td>
<td>0.877</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.1</td>
<td>0.950</td>
<td>0.947</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>0.963</td>
<td>0.973</td>
<td></td>
</tr>
<tr>
<td>75( \mu )m 95% passing</td>
<td>5.5</td>
<td>0.852</td>
<td>0.853</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.1</td>
<td>0.912</td>
<td>0.915</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>0.934</td>
<td>0.955</td>
<td></td>
</tr>
</tbody>
</table>

*Environmental Progress (Vol. 12, No. 3)*

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and the tank, which are related to pH values at the bottom of the wetted-wall column and at the tank respectively. The dissolution rate constants of many limestones gather along the primary straight line of $10^{-m}$. The results indicate that the dissolution rate equation in this study is applicable to limestone of various particle sizes, composition and place of production. These data were processed by the method of non-linear least squares and $k_a = 7.14 \times 10^{-9}$ was obtained. This $k_a$ value is larger than the $k_a$ value obtained in either batch or continuous type test because chloride ions accumulated in the liquid and might reduce the $k_a$ value in wetted-wall column test.

**CONCLUSIONS**

In this study, the dissolution kinetics of limestone in the FGD process were examined, and the following results were obtained: (1) The dissolution rate equation introduced by the mass transfer rate in an agitated fluid gives results in good agreement with the measured values of dissolution rate and the reduction rate of the particle size distribution of unreacted limestone in both batch and continuous type tests. (2) The above dissolution rate equation gives values also in good agreement with the measured values of dissolution rate and the size distribution of unreacted limestone in both batch and continuous type tests. (3) According to this evaluation, it is possible to calculate the reactivity of high calcium limestone with specified level of the particle size distribution and design the FGD process more accurately.

**NOTATION**

- $B$ = enhancement factor [m$^{-1}$]
- $\Delta C$ = concentration gradient [kgmol/m$^3$]
- $D$ = diffusion coefficient [m$^2$/s]
- $d_p$ = particle size of limestone [m]
- $F$ = overall fraction of unreacted limestone [-]
- $f$ = fraction of unreacted limestone [-]
- $k_a$ = dissolution rate constant (corrected by pH value) [m$^2$/s]
- $k_c$ = dissolution rate constant [m$^2$/s]
- $k_L$ = mass transfer coefficient [m/s]
- $Sc$ = Schmidt number ($v_c/D$) [-]
- $Sh$ = Sherwood number ($k_L-d_p/D$) [-]
- $t$ = time [s]
- $V$ = initial volume of limestone particle [m$^3$]
- $V_p$ = volume of limestone particle [m$^3$]
- $\epsilon$ = agitation power per unit weight of fluid [W/kg]
- $\eta$ = overall fraction of dissolved limestone [-]
- $\nu_c$ = kinematic viscosity of fluid [m$^2$/s]
- $\rho_f$ = density of fluid [kg/m$^3$]
- $\rho_m$ = molar density of limestone [kgmol/m$^3$]
- $\tau$ = average residential time [s]
- $\phi_j$ = fraction of limestone with initial diameter $d_{j0}$ [m]

**Subscripts**

- $B$ = batch reaction system
- $C$ = continuous reaction system
- $j$ = jth particle group

**LITERATURE CITED**
