LIMESTONE DISSOLUTION IN WET FLUE GAS DESULPHURIZATION

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ABSTRACT
The wet type limestone (CaCO₃) scrubbing process is the most commonly used flue gas desulphurization process for treatment of waste gases from power stations and incineration plants. Accurately evaluating the dissolution rate of CaCO₃ is important in the development and the efficient operation of the wet scrubbing. Parameters influencing the CaCO₃ dissolution and SO₂(g) absorption were measured using the jacked stirred vessel in conditions close to the flue gas desulphurization system. The results of the investigations show that the CaCO₃ dissolution is controlled by H⁺ diffusion at lower pH (pH 4) while at higher pH (pH 5 to 6), the contribution of OH⁻ dominates the reactions. The dissolution rate is higher for smaller particle size but the rate of dissolution also depends on impurities in the CaCO₃ (e.g. insoluble salts). Inorganic additives such as Na₂SO₄, NaCl, MgSO₄, and MgCl₂ only slightly influence the dissolution, but buffer substances such as Na₂SO₃ and NH₄Cl clearly enhance the dissolution rate as well as organic additives such as adipic and acetic acid.

INTRODUCTION
The CaCO₃ slurry is used to absorb sulphur dioxide (SO₂(g)) from the flue gas in the scrubbing process of flue gas desulphurization (FGD) plants. The dissolution of CaCO₃ influences the effectiveness of the process. A poor CaCO₃ utilization can impair the SO₂(g) removal capability of the absorber. The CaCO₃ dissolution experiments have been conducted by using a stirred vessel to identify the factors which effect the dissolution. The dissolution process is tracked by adding a strong acid to a stirred CaCO₃ slurry using pH static method. The effects of the various conditions on the limestone dissolution are investigated in SO₂(g) absorption experiments in a stirred vessel and in a spray tower.

The solution composition when CaCO₃ slurry dissolves completely in a stirred vessel can be calculated by a system of fundamental equations, i.e. the appropriate set of equations comprises the equilibrium constant relationships and electroneutrality [7]. Species involved in the system are CO₂(aq), HCO₃⁻, CO₃²⁻, H⁺, OH⁻, Ca²⁺, and additives represented by species from diprotic acids (H₂A, HA⁻ and A²⁻) and monoprotic acids (HA and A⁻). If CaCO₃ slurry is used to absorb the SO₂(g), additional species (i.e. SO₂(aq), HSO₃⁻ and SO₃²⁻) are involved in the equilibrium. In the driving force estimation of the absorption process, the amount of dissolved gas is calculated according to Henry’s law. The activity coefficient (γ) is calculated based on the expression of individual activity coefficients from the extended Debye Hückel formula. The dissolution process of CaCO₃ slurry can be influenced by various operating conditions and the soluble ions in the solution. Some of these ions such as Cl⁻ and Ca²⁺ are normally present in FGD system, other inorganic or organic additives are usually added to enhance FGD system performance.
EXPERIMENTAL APPARATUS
The CaCO₃ dissolution under static pH and the SO₂(g) absorption in CaCO₃ slurry are conducted using a stirred batch reactor (Figure 1) according to the type of experiment illustrated in Table 1. The SO₂(g) scrubbing by CaCO₃ slurry is implemented in a counter current SO₂(g) scrubber pilot scale (Figure 2).

In the CaCO₃ dissolution experiment, the cumulative volume of the added acid (HCl) is recorded as a function of time. In SO₂ absorption by CaCO₃ slurry, the SO₂-N₂ bubbles are introduced in the CaCO₃ slurry and the change of pH versus time is recorded by the titrino.

(I) Stirred Reactor, D = 13 cm, L = 15 cm, V= 1000 mL;
(II) Automatic Titration  (titrino)
(III) Gas Source (N₂ and SO₂)
(IV) Thermostat DC10
(V) Computer, software VESUV 3.0

**Figure 1.** The stirred reactor and the analytical apparatus

<table>
<thead>
<tr>
<th>No</th>
<th>Type of experiments</th>
<th>The operating conditions</th>
<th>CaCO₃ (0.5 gram/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Static pH</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>1.</td>
<td>Agitation</td>
<td>5, 5.2</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>pH and temperature</td>
<td>4, 5, 6</td>
<td>25, 50, 75</td>
</tr>
<tr>
<td>3.</td>
<td>pH and particle size</td>
<td>4, 5, 6</td>
<td>50</td>
</tr>
<tr>
<td>4.</td>
<td>Inorganic additives</td>
<td>CaCl₂, NaCl, MgCl₂, MgSO₄, NaSO₄, NH₄Cl, Na₂SO₃ (IS 3, 30, 112.5) NaSO₄ (IS, 3, 9, 15, 30, 45, 60, 112.5)</td>
<td>5.2</td>
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<tr>
<td>5.</td>
<td>Organic Additives</td>
<td>C₆H₁₀O₄ - Adipic acid, C₂H₄O₂ - Acetic acid (IS 3, 30, 112.5)</td>
<td>4.75, 5.2, 6.0</td>
</tr>
<tr>
<td>6.</td>
<td>SO₂ absorption (1520 ppm), P=1 bar, F=0.2L/min</td>
<td>55</td>
<td>500</td>
</tr>
</tbody>
</table>

**Table 1.** The type of stirred vessel experiments, the operating conditions, and the CaCO₃ sources (HCl concentration = 0.2 mol/L; IS = ionic strength in mM)
The scrubber pilot scale consists of a pipe with 150 mm width of inner diameter and the length of 2000 mm. The CaCO$_3$ slurry is sprayed counter currently to the flue gas. For a certain liquid/gas ratio, the raw gas and suspension at a certain temperature are simultaneously introduced to the column. The required pH value of the suspension is set up by dosing CaCO$_3$ slurry. In the beginning the raw gas is measured using online measurement. After the measured gas input is stable enough, the online measurement is switched to measure the cleaned gas. The concentration difference between raw gas and cleaned gas is used to determine the efficiency of the scrubber.

SO$_2$(g) concentration in the raw gas : 1000 and 2000 ppm
pH value of the CaCO$_3$-gypsum suspension : 5.5 and 6
L/G ratio : 6, 10, 13, 16
Raw gas flowrate : 100, 130, 160 m$^3$/h
Temperature in the scrubber : 55°C

**Figure 2. The SO$_2$(g) Scrubber Pilot Scale**

**RESULT AND DISCUSSION**

As for the influence of pH on the dissolution, the results show agreement with most of literatures, i.e. the dissolution rate is a strong function of the pH. The lower the pH, the higher the observed rate and also the quicker the system in reaching saturation condition. Inorganic additives such as Na$_2$SO$_4$, NaCl, MgSO$_4$, and MgCl$_2$ at ionic strength (IS) 112.5 mM only slightly influence the dissolution (Figure 3a), similar results were also obtained by [3]. Significant dissolution retardation occurs when CaCl$_2$ is added, this is also shown in [1], [2] and [3]. Excess Ca$^{2+}$ decreases the solubility of CaCO$_3$ at the CaCO$_3$ surface.

The dissolution rate enhancement occurs when NH$_4$Cl or Na$_2$SO$_3$ (Figure 3b) is added. Inhibition by Na$_2$SO$_3$ as described in [3] can not be observed until an IS 112.5 mM is reached. Organic additives, such as adipic acid and acetic acid (Figure 4a and 4b), are also capable of increasing the dissolution rate and no inhibition until IS 112.5 mM is detected. These findings are in contrast to [2] and [3], where it is stated that adipic acid shows minor inhibition in the CaCO$_3$ dissolution. The increasing dissolution rate by additives is usually connected with the buffer capacity, see [1] and [6]. The general explanation is that the released hydroxide ions are buffered keeping thereby the pH at a lower level in the vicinity of the particles. Buffer substances also considerably increase the SO$_2$(g) absorption rate by keeping the pH low enough for a fast limestone dissolution and high enough for good SO$_2$(g) absorption.

There are, however, some more interesting effects related with buffer solutions, which have been investigated in more detail. The first is the use of buffer substances at a pH when the buffer capacity approaches zero. For instance, the buffer capacity of Na$_2$SO$_3$ at a pH of about 4.5 is virtually zero (Figure 5a), but even at this pH the limestone dissolution rate is notably increased by the addition of Na$_2$SO$_3$ (Figure 3b). An explanation could be, that although
the pH is kept constant (pH static method) at a macroscopic level, it might increase on a microscopic level around the limestone particle; when no buffer substances are present the pH near the limestone surface could even reach the equilibrium value ($\approx 8.2$), whereas with Na$_2$SO$_3$ presents the pH possibly does not rise higher than about 6.

Another interesting phenomena is the reversal of the pH dependence of the dissolution rate at high concentrations of buffer substances. Usually the limestone dissolution increases with decreasing pH, but at higher concentrations of additives, this order could be reversed, as is shown in Figure 5b.1, 5b.2, & 5b.3 for adipic acid. The same behaviour was observed with other organic, but not with inorganic buffer substances. No explanation for this effects could be found yet.

Other results indicate that temperature has a more significant influence than agitation speed for the dissolution rate, similar results can be found in [1] and [4]. Since the dissolution of CaCO$_3$ is an endothermic reaction, the entropy as the principal driving force increases when temperature rises, resulting in the shift of the reaction towards more products, which means that more CaCO$_3$ dissolves. As for the particle size distribution, smaller particles generally have a higher dissolution rate (Figure 6a), but converse results are found in [5] and [6] where dissolution is independent of particle size.

The results of SO$_2$(g) absorption with CaCO$_3$ slurry experiment indicate clearly the influence of CaCO$_3$ in increasing the capacity of the solution to neutralize the dissolved SO$_2$(aq) (Figure 6b). The existence of CaCl$_2$ and NaCl show different effects in SO$_2$(g) absorption process. At a high Ca$^{2+}$ content the concentration gradient of Ca$^{2+}$ between the particle surface and the bulk becomes small and reduces the rate of CaCO$_3$ dissolution. The influence of NaCl (the same ionic strength as CaCl$_2$) is significant when buffer capacity from CaCO$_3$-CO$_2$(aq) runs out, and slight extension of buffer capacity occurs. To have a further insight in limestone dissolution, experiments are now being run under chemisorption condition in a pilot scale scrubber column.
**Figure 4.** The remaining fraction of CaCO₃ under influence of organic additives, at pH 5.2, T 25°C, stirrer speed 500 rpm, IS in mM

**Figure 5.** (a). Buffer capacity curves, (b). the remaining fraction of CaCO₃ at various IS of adipic acid and pH, T 25°C, stirrer speed 500 rpm, IS in mM
CONCLUSION

The dissolution of CaCO₃ is proved to be influenced by various operating conditions, i.e. pH-temperature-agitation, physical properties (e.g. particle size) - chemical properties (e.g. insoluble salts) of the CaCO₃ particles, as well as solution composition (additional inorganic-organic species). The main factors which influence the dissolution rate are the pH and additions of certain additives which effect the buffer capacity of the solution. Interesting results are found for the addition of Na₂SO₃ when an increase of the dissolution rate is still observed although its buffer capacity approaches zero, and for additions of organic additives (adipic acid and acetic acid) when a reversal of the pH dependence at high concentrations of buffer substances occurs. Further investigations are still required to provide reliable and unambiguous data of CaCO₃ dissolution, since inconsistencies between literature data and current results are still observed.

REFERENCE