

LIMESTONE DISSOLUTION IN WET FLUE GAS DESULPHURIZATION

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ABSTRACT

The wet type limestone (CaCO_3) 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 CaCO_3 is important in the development and the efficient operation of the wet scrubbing. Parameters influencing the CaCO_3 dissolution and $\text{SO}_{2(g)}$ absorption were measured using the jacketed stirred vessel in conditions close to the flue gas desulphurization system. The results of the investigations show that the CaCO_3 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 CaCO_3 (e.g. insoluble salts). Inorganic additives such as Na_2SO_4 , NaCl , MgSO_4 , and MgCl_2 only slightly influence the dissolution, but buffer substances such as Na_2SO_3 and NH_4Cl clearly enhance the dissolution rate as well as organic additives such as adipic and acetic acid.

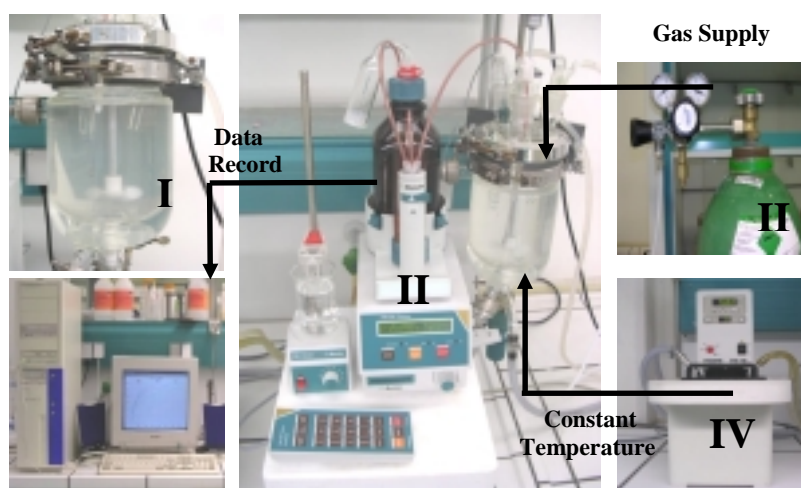
INTRODUCTION

The CaCO_3 slurry is used to absorb sulphur dioxide ($\text{SO}_{2(g)}$) from the flue gas in the scrubbing process of flue gas desulphurization (FGD) plants. The dissolution of CaCO_3 influences the effectiveness of the process. A poor CaCO_3 utilization can impair the $\text{SO}_{2(g)}$ removal capability of the absorber. The CaCO_3 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 CaCO_3 slurry using pH static method. The effects of the various conditions on the limestone dissolution are investigated in $\text{SO}_{2(g)}$ absorption experiments in a stirred vessel and in a spray tower.

The solution composition when CaCO_3 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 $\text{CO}_{2(aq)}$, HCO_3^- , CO_3^{2-} , H^+ , OH^- , Ca^{2+} , and additives represented by species from diprotic acids (H_2A , HA^- and A^{2-}) and monoprotic acids (HA and A^-). If CaCO_3 slurry is used to absorb the $\text{SO}_{2(g)}$, additional species (i.e. $\text{SO}_{2(aq)}$, HSO_3^- and SO_3^{2-}) 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 CaCO_3 slurry can be influenced by various operating conditions and the soluble ions in the solution. Some of these ions such as Cl^- and Ca^{2+} are normally present in FGD system, other inorganic or organic additives are usually added to enhance FGD system performance.

EXPERIMENTAL APPARATUS

The CaCO_3 dissolution under static pH and the $\text{SO}_{2(g)}$ absorption in CaCO_3 slurry are conducted using a stirred batch reactor (Figure 1) according to the type of experiment illustrated in Table 1. The $\text{SO}_{2(g)}$ scrubbing by CaCO_3 slurry is implemented in a counter current $\text{SO}_{2(g)}$ scrubber pilot scale (Figure 2).



In the CaCO_3 dissolution experiment, the cumulative volume of the added acid (HCl) is recorded as a function of time. In SO_2 absorption by CaCO_3 slurry, the $\text{SO}_2\text{-N}_2$ bubbles are introduced in the CaCO_3 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 (N_2 and SO_2)
- (IV) Thermostat DC10
- (V) Computer, software VESUV 3.0

Figure 1. The stirred reactor and the analytical apparatus

No	Type of experiments	The operating conditions			CaCO_3 (0.5 gram/L)
		Static pH	Temp. ($^{\circ}\text{C}$)	Stirrer (rpm)	
1.	Agitation	5, 5.2	50	250, 500, 750, 1000, 1250	Calciglos, OMC2, OMC15, CaCO_3 99%
2.	pH and temperature	4, 5, 6	25, 50, 75	500	Calciglos, OMC2, OMC15, CaCO_3 99%, Voitsberg
3.	pH and particle size	4, 5, 6	50	500	Calciglos, OMC2, OMC15, CaCO_3 99%
4.	Inorganic additives: CaCl_2 , NaCl , MgCl_2 , MgSO_4 , Na_2SO_4 , NH_4Cl , Na_2SO_3 (IS 3, 30, 112.5) Na_2SO_3 (IS, 3, 9, 15, 30, 45, 60, 112.5)	5.2	25, 50	500	Voitsberg
		5.2	25	500	Voitsberg
5.	Organic Additives: $\text{C}_6\text{H}_{10}\text{O}_4$ - Adipic acid, $\text{C}_2\text{H}_4\text{O}_2$ - Acetic acid (IS 3, 30, 112.5)	4.75, 5.2, 6.0	25	500	
6.	SO_2 absorption (1520 ppm), P=1 bar, F=0.2L/min		55	500	Voitsberg

Table 1. The type of stirred vessel experiments, the operating conditions, and the CaCO_3 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.

$\text{SO}_{2(g)}$ 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 $\text{SO}_{2(g)}$ 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_2SO_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_4Cl or Na_2SO_3 (Figure 3b) is added. Inhibition by Na_2SO_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 $\text{SO}_{2(g)}$ absorption rate by keeping the pH low enough for a fast limestone dissolution and high enough for good $\text{SO}_{2(g)}$ 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_2SO_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_2SO_3 (Figure 3b). An explanation could be, that although

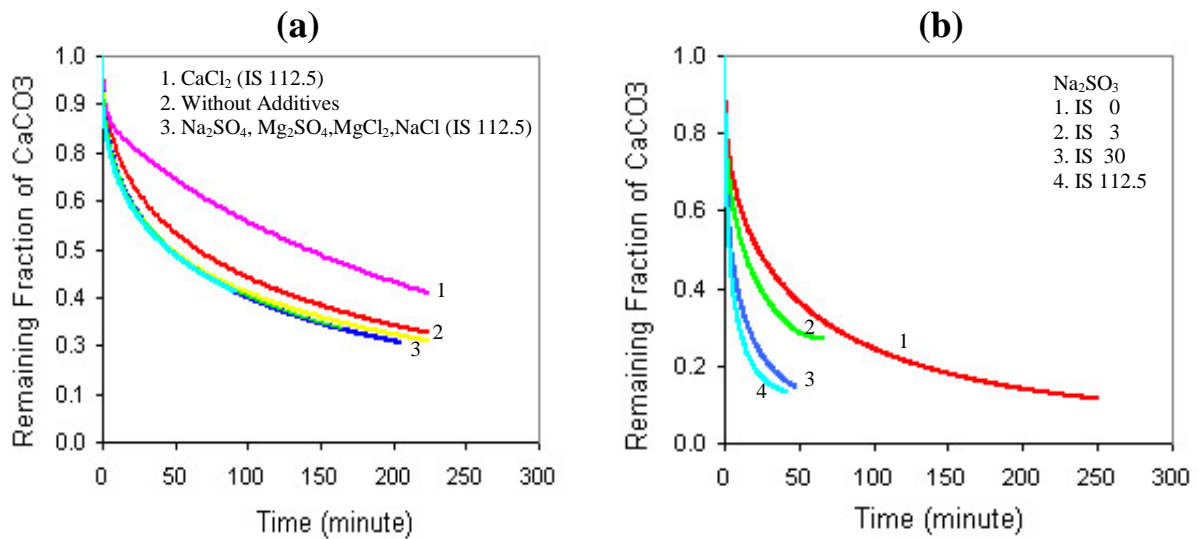


Figure 3. The remaining fraction of CaCO_3 under influence of inorganic additives, at T 50°C , stirrer speed 500 rpm, IS in mM, pH 5.2 for (a) and pH 4.75 for (b).

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 (≈ 8.2), whereas with Na_2SO_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 $\text{SO}_{2(g)}$ absorption with CaCO_3 slurry experiment indicate clearly the influence of CaCO_3 in increasing the capacity of the solution to neutralize the dissolved $\text{SO}_{2(aq)}$ (Figure 6b). The existence of CaCl_2 and NaCl show different effects in $\text{SO}_{2(g)}$ 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 $\text{CaCO}_3\text{-CO}_{2(aq)}$ 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.

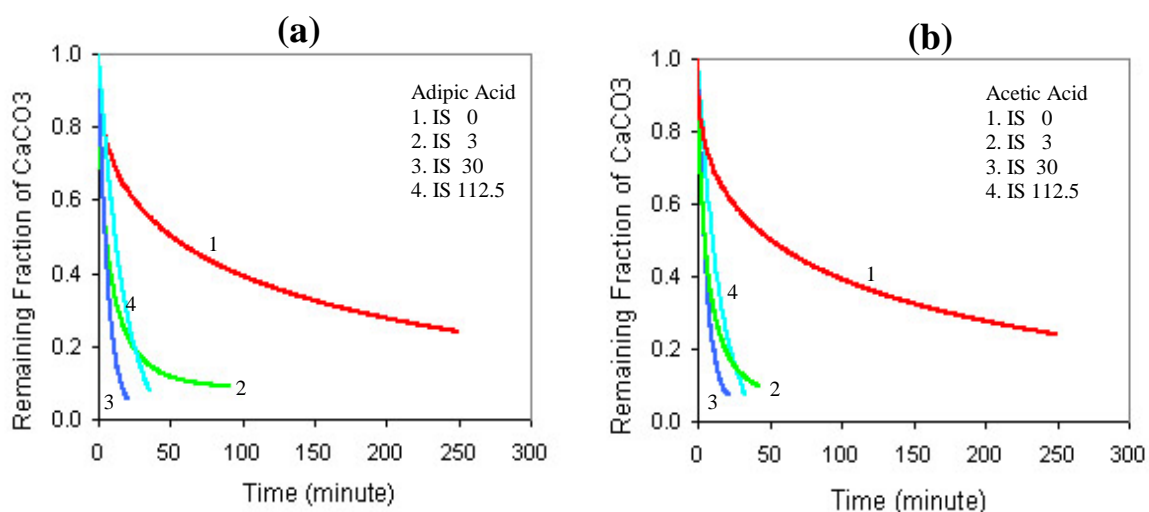


Figure 4. The remaining fraction of CaCO_3 under influence of organic additives, at pH 5.2, T 25°C, stirrer speed 500 rpm, IS in mM

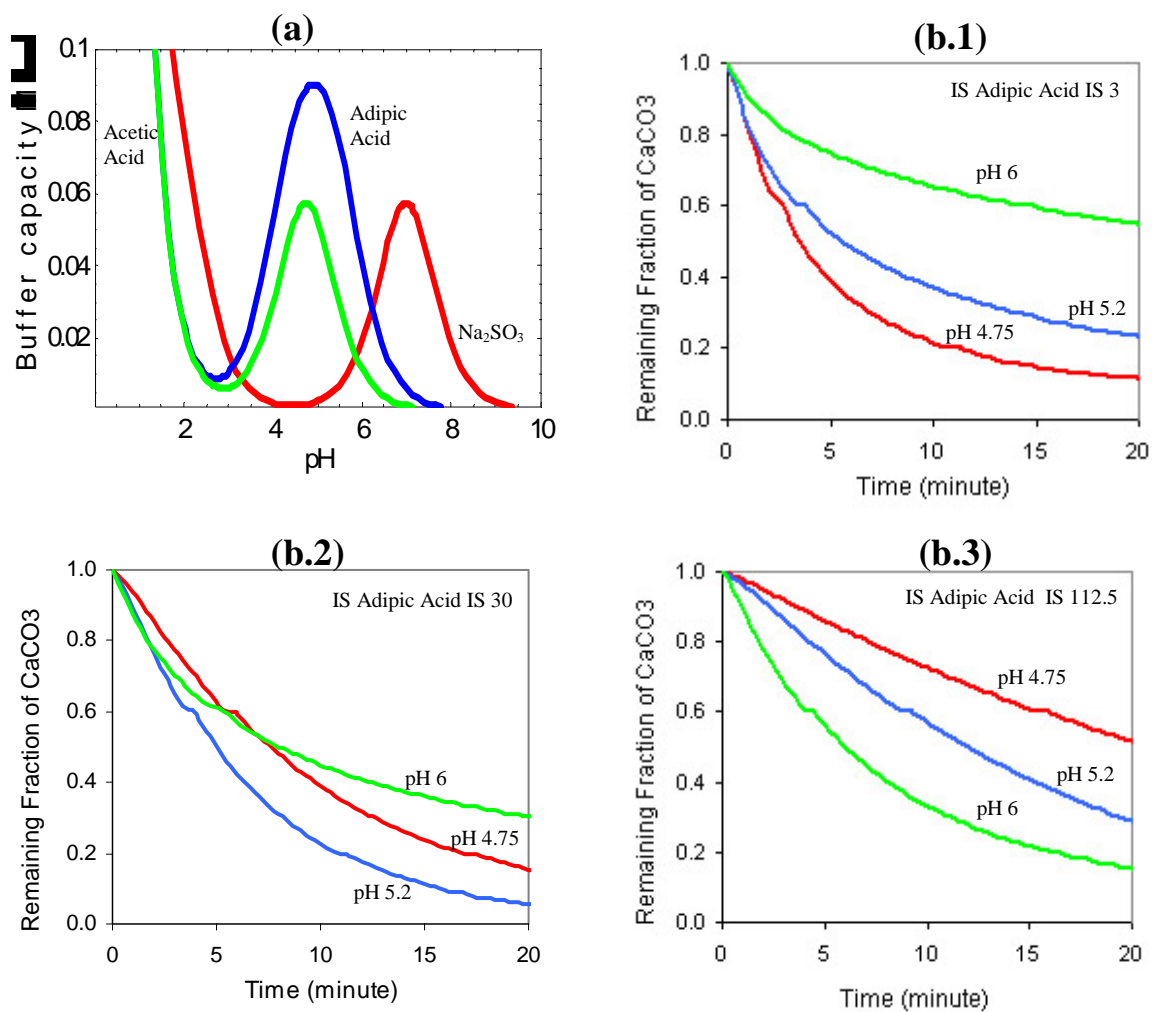


Figure 5. (a). Buffer capacity curves, (b). the remaining fraction of CaCO_3 at various IS of adipic acid and pH, T 25°C, stirrer speed 500 rpm, IS in mM

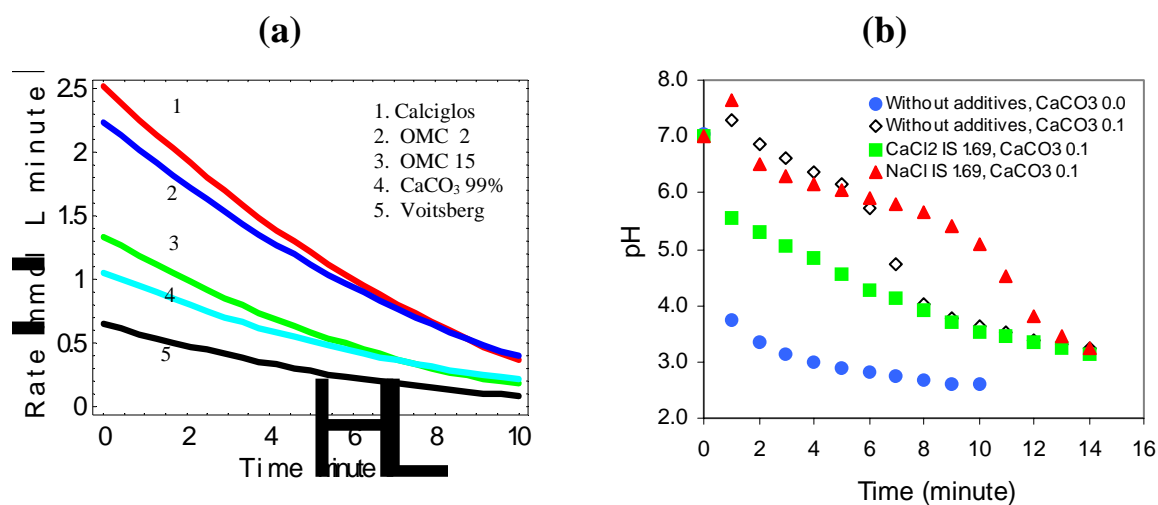


Figure 6. (a) The dissolution rate of various CaCO₃ sources, at pH 5.2, T 50°C, stirrer speed 500 rpm, $dp_{\text{Calciglos}} < dp_{\text{OMC2}} < dp_{\text{CaCO}_3\text{-99\%}} < dp_{\text{OMC15}} < dp_{\text{Voitsberg}}$ (b) the SO_{2(g)} absorption, at T 55°C, IS in M, CaCO₃ in g/L

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

- [1] Chan P.K and Rochelle G.T., "*Limestone Dissolution Effects of pH, CO₂, and Buffers Modelled by Mass Transfer*", American Chemical Society, 1982
- [2] Hunek B. and Gal. E., "*The Effect of Additives, Ion Concentration and pH on Limestone Dissolution*", General Electric Environmental Services, Lebanon, 1994
- [3] Jarvis J.B. et al., "*Development of a Predictive Model for Limestone Dissolution in Wet FGD Systems*", Presentation at the EPA/EPRI first Combined FGD and Dry SO₂ Control Symposium, St Louis USA, 1988
- [4] Meserole R. M., Glover R.L., and Steward D.A., "*Studies of Major Factors Affecting Magnesium Limestone Dissolution*", American Chemical Society, 1982
- [5] Shin-Min S. et al., "*Dissolution Rates of Limestone of Different Sources*", Journal of Hazardous Materials, 2000
- [6] Stergarsek A. et al., "*Modelling and Experimental Measurement of Limestone Dissolution under Enhance Wet Limestone FGD Process Conditions*", Acta Chim. Slovenia, 1999
- [7] Stumm W. and Morgan J.J., "*Aquatic Chemistry – Chemical Equilibria and Rates in Natural Waters*", Third Edition, John Wiley and Sons Inc., Canada, 1996