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Dissolution rate of South African calcium-based materials at constant pH

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ABSTRACT

One of the most important steps in the wet limestone–gypsum flue gas desulphurization (WFGD) process is limestone dissolution, which provides the dissolved alkalinity necessary for SO_2 absorption. Accurately evaluating the limestone dissolution rate is important in the design and efficient operation of WFGD plants. In the present work, the dissolution of limestone from different sources in South Africa has been studied in a pH-Stat apparatus under conditions similar to those encountered in wet FGD processes. The influence of various parameters such as the reaction temperature ($30 \le T \le 70\,^{\circ}C$), sorbent particle size ($25 \le dp \le 63\,\mu m$), solution acidity ($4 \le pH \le 6$), and chemical composition were studied in order to determine the kinetics of the sorbent dissolution. The results obtained indicate that the dissolution rate increased with a decrease in particle size, decrease in pH and an increase in temperature. Kinetic analysis of the results indicates that the dissolution of limestone is according to the shrinking core model with surface control, i.e. $1-(1-3)^{1/3} = kt$.

1. Introduction

The electricity sector plays a pivotal role in the South African economy. South Africa's generating technology is based largely on coal-fired power stations, and at the end of 1999, there were 49 power stations in the country, of which 20 were coal-fired accounting for 90% of the total capacity of 43,142 MW [1]. On combustion, the sulphur contained in the fuel is converted to SO_2. To a large extent, the SO_2 is subsequently converted into H_2SO_4, a precursor of acid rain. The serious environmental and health problems caused by high SO_2 emissions into the atmosphere have encouraged the study of ways of reducing their levels in the flue gas.

Flue gas desulphurization (FGD) is the widest applied measure for SO_2 emissions reduction [2]. There are many FGD methods that have been developed of which the wet flue gas desulphurization (WFGD) is the most widespread. In the wet FGD process, limestone slurry is used to absorb SO_2 to form solid products. There are several reactions and physical steps which may affect the rate of SO_2 absorption within a limestone slurry. These include [3]:

(a) The diffusion of SO_2 through the gas film near the gas-liquid interface.
(b) The dissolution of SO_2 in the liquid phase.
(c) The first dissociation of SO_2.
(d) The second dissociation of SO_2.
(e) The dissolution of $CaCO_3$.
(f) The diffusion of SO_2 and the different ions towards the reaction area of the liquid film.

Step (a) above depends largely on the operating conditions and the type of equipment used to obtain contact between the phases. Steps (b)–(d) are virtually instantaneous. The dissolution rate of the $CaCO_3$ plays an important role in the overall kinetics and may be the rate controlling step in the SO_2 absorption. Thus accurately evaluating the dissolution rate of the limestone is important in the development and the efficient operation of the SO_2 wet scrubbing system.

The dissolution kinetics of calcium carbonate has been widely studied for many years. However, a large number of papers published have been concerned with how the dissolution process affects geological processes such as diagenesis of calcareous deep-sea sediments, formation of karst in limestone terranes, the evolution of water chemistry in calcite depositing stream systems, and the global CO_2 cycle [4–6]. Recently, several researchers have studied the dissolution of limestone with special reference to the conditions encountered in the wet type FGD process. Shih et al. [7] investigated the dissolution rate of six limestone samples from different sources in a pH-Stat apparatus at pH 4 and 6. Their results indicated that the dissolution rate was controlled by the mass transfer of hydrogen ions accompanied by chemical reactions in the liquid film surrounding the limestone particle. The measured value of the mass transfer coefficient increased with

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Nomenclature

$a_{H^+,\mathrm{surf}}$	hydrogen ion activity at the surface of the sorbent
$a_{H^+,\mathrm{bulk}}$	hydrogen ion activity in the bulk solution
C_A	bulk concentration (mol cm^{-3})
E	activation energy (kJ mol^{-1})
k	reaction rate constant (s^{-1})
k_1	mass transfer coefficient (ms^{-1})
R	universal gas constant (kJ mol^{-1} K^{-1})
R_B	initial sorbent particle radius (m)
t	reaction time (s)
T	temperature (K)
$X_B = X$	fraction of dissolved sorbent (−)
k_0	pre-exponential factor

Greek letter

ρ_B	molar density of sorbent (kg mol m^{-3})

an increasing pH value and stirrer speed but remained constant with particle size. Using a sequential pH–time derivative method, Ahlbeck et al. [8] observed that the dissolution rate of limestone is controlled by both liquid film diffusion and chemical reaction. There is a correlation between the apparent limestone porosity and the dissolution kinetics [9]. Using eight limestone samples, they showed that the reaction half-time in pH-Stat apparatus reduced with an increase in the apparent porosity. Hosten and Gulsun [10] showed that the particle size and dolomite content of the limestone were the most influential parameters in the reactivity measurements. Given the critical importance of the limestone dissolution in the desulphurization process, studies have been carried out on ways of increasing the limestone dissolution by the use of various additives such as organic acids. The organic acids which have been tested with good results include adipic acid [11], formic acid [12], and dibasic acid [13]. The use of ammonium salts [14] have also been shown to improve the limestone dissolution.

Several methods have been developed for the evaluation of the suitability of limestone for the sulphation process. They are based on the reaction of limestone with gaseous SO_2 or an aqueous solution of SO_2, i.e. H_2SO_3 or H_2SO_4. When strong acids like sulphuric acid or hydrochloric acid are used, the reaction mechanism is close to that in a wet FGD plant equipped with air oxidation of the bisulphite ion. If an absorbent slurry sample in a stirred beaker is neutralized by a strong acid, the dissolution rate can be ascertained by measuring the absorbent conversion as a function of time at constant pH. Recently, ASTM developed a standard test method for the determination of total neutralizing capability of dissolved calcium and magnesium oxides in lime for flue gas desulphurization (ASTM C:1318-95). This method also recommends an acid titration procedure.

2. Materials and methods

2.1. Materials

Natural limestone and dolomite samples from different mines in South Africa were provided by different quarries. The $CaCO_3$ contents of these materials ranged from 44 to 92 wt.%, and the magnesium carbonate content varied from 1.26 to 39.0 wt.% as shown in Table 1.

The percentage available for dissolution in a given sample was taken as the sum of the $CaCO_3$ and the $MgCO_3$.

Table 1
Chemical analysis of sorbent materials used

Component	A (%)	LYT (%)	GW (%)	LD (%)	LL (%)
SiO_2	5.95	4.48	13.33	–	–
Al_2O_3	1.53	0.36	1.67	–	–
Fe_2O_3	1.83	1.61	0.67	–	–
CaO	88.39	53.54	81.67	44	92.4
MgO	1.26	36.52	1.67	39.0	1.75
Combustible matter	38.3	45.60	40	–	–

2.2. Methods

Batch dissolution rates for various calcium-based materials were measured at constant pH by using a pH-Stat apparatus. The pH was automatically controlled by titrating with a 1 M HCl solution. The limestone dissolution rate was related to the titration rate by the stoichiometric equation:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1)$$

1.5 g of sample material was dissolved in 200 mL of distilled water. The cumulative dissolution was determined directly from a recording of HCl added vs. time. The fraction of dissolution was obtained by the ratio of the HCl added volume to that required for complete dissolution.

The experimental apparatus is shown in Fig. 1. Agitation was provided by a three-blade stirrer rotating at 100 rpm. The reactor temperature was controlled by a temperature controlled water bath. The pH in the reaction vessel was measured using a pH electrode inserted in the solution and connected to a pH 200 1/8 DIN pH/ORP controller supplied by Eutech Instruments. The controller has a specified pH range of 0.00–14.00 and a resolution/accuracy of pH ±0.01. When the pH exceeds the set value, a peristaltic pump is activated to add acid to the reaction vessel and reduce the pH to the desired value. Most of the experiments were performed at 50 °C except for those done to determine the influence of reaction temperature.

3. Kinetic analysis

In a fluid–solid system, the reaction rate may be generally controlled by one of the following steps; diffusion through the fluid film, diffusion through the ash, or chemical reaction at the surface of the core of unreacted materials [15]. The rate of the process is controlled by the slowest of these sequential steps. In order to determine the kinetic parameters and the rate controlling step for

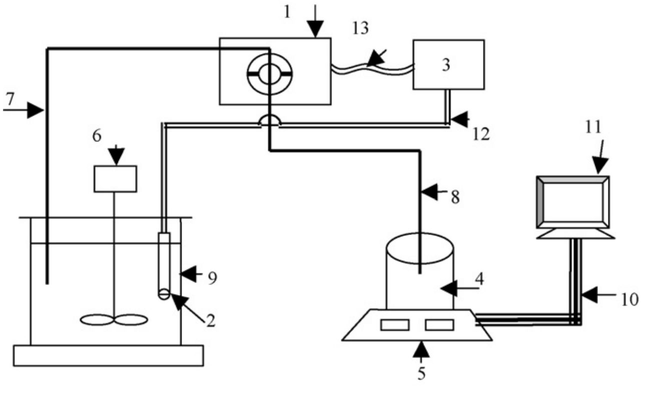

Fig. 1. Schematic drawing of the experimental set-up. (1) Peristaltic pump, (2) pH electrode, (3) pH controller, (4) acid solution beaker, (5) electronic balance, (6) stirrer, (7,8) plastic tubing, (9) reaction vessel, (10) RS232 cable, (11) computer work station, (12) wiring for pH electrode, (13) connection between pump and controller.