



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

Z.O. Siagi*, M. Mbarawa

Department of Mechanical Engineering, Pretoria Campus, Tshwane University of Technology, Private Bag X680, 0001, Pretoria, South Africa

ARTICLE INFO

Article history:

Received 27 July 2007

Received in revised form 6 May 2008

Accepted 4 July 2008

Available online 11 July 2008

Keywords:

Desulphurization

Dissolution

pH-Stat

Sorbent

Limestone

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 ($30 \leq T \leq 70^\circ\text{C}$), sorbent particle size ($25 \leq dp \leq 63 \mu\text{m}$), solution acidity ($4 \leq \text{pH} \leq 6$), 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. $1 - (1 - 3)^{1/3} = kt$.

© 2008 Published by Elsevier B.V.

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]:

- The diffusion of SO_2 through the gas film near the gas-liquid interface.
- The dissolution of SO_2 in the liquid phase.

- The first dissociation of SO_2 .
- The second dissociation of SO_2 .
- The dissolution of CaCO_3 .
- 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

* Corresponding author. Tel.: +27 123825931; fax: +27 123825602.
E-mail address: siagiz@tut.ac.za (Z.O. Siagi).

Nomenclature

$a_{\text{H}^+, \text{surf}}$	hydrogen ion activity at the surface of the sorbent
$a_{\text{H}^+, \text{bulk}}$	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 ($\text{kJ mol}^{-1} \text{K}^{-1}$)
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:



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 $\text{pH} \pm 0.01$. 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

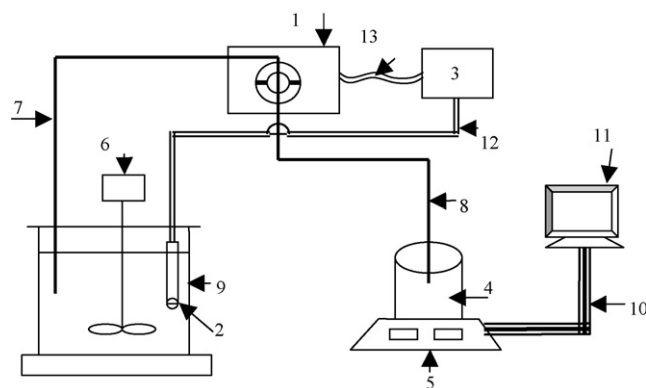


Fig. 1. Schematic drawing of the experimental set-up. (1) Peristaltic pump, (2) pH electrode, (3) pH controller, (4) acid solution beaker, (5) electronic balance, (6) stirrer, (7,8) plastic tubing, (9) reaction vessel, (10) RS232 cable, (11) computer workstation, (12) wiring for pH electrode, (13) connection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

the dissolution of limestone, the experimental data are analyzed on the basis of the sharp interface or shrinking core model (SCM). The SCM assumes that the reaction occurs initially at the particle outer surface then moves towards the centre of the particle by means of a narrow reaction front. This model is suitable for a simple reaction of a fluid with a non-porous solid that does not undergo any structural changes. This reaction model between a fluid (A) and a solid (B) may be represented by:



As no ash covers the unreacted core as the reaction proceeds, there can be only two controlling steps, namely, fluid film diffusion or chemical reaction.

If the process is controlled by resistance of the fluid layer, then:

$$t = \frac{\rho_B R}{3bk_1 C_A} X_B \quad (3)$$

If the process is controlled by resistance of chemical reaction, then:

$$t = \frac{\rho_B R}{bk_s C_A} [1 - (1 - X_B)^{1/3}] \quad (4)$$

or

$$1 - (1 - X_B)^{1/3} = kt \quad (5)$$

In the current study, the fit of all the experimental data into the integral rate is tested and the multiple regression coefficients obtained for the integral rate expression are calculated. A plot of $1 - (1 - X)^{1/3}$ vs. time for each sorbent material can be represented by a straight line if the reaction is chemically controlled. The values of k is then calculated from the slope of the straight line corresponding to each material

The temperature effect on the dissolution rate is often a unique indication of the reaction mechanism itself. For example, diffusion-controlled reactions in solutions have activation energies ($E_a < 20$ kJ/mol) that are lower than those for surface controlled reactions (40–80 kJ/mol). Therefore the accurate estimation and interpretation of the activation energy value is important [16]. A number of recent studies have analyzed the temperature dependence of mineral dissolution rates. The temperature dependence of the dissolution rate typically follows the Arrhenius law:

$$k = k_0 e^{-E/RT} \quad (6)$$

which is grounded in statistical mechanics and quantum theory. In this equation, k_0 is the pre-exponential factor, E is the activation energy of the overall mineral-fluid reaction, R is the gas constant, and T is the temperature. Activation energy is currently estimated from experimental rate values of dissolution reactions conducted at different temperatures. The values of k_0 and E can be obtained from the straight line plot of $\ln k$ vs. $1/T$.

4. Results and discussion

4.1. Effect of particle size

Three size fractions of sample A were used to determine the influence of the particle size on the dissolution rate. The size fractions are A1 ($-25 \mu\text{m}$), A2 ($-45 \mu\text{m}$) and A3 ($-63 \mu\text{m}$). Fig. 2 shows the data of HCl volume added vs. time at 50°C and pH 5 for the three size fractions of sample A. The results show that the limestone conversion is a strong function of the particle size; the finer the particle size is, the higher the conversion within the same time period. For all the three size fractions investigated, there was a high initial consumption of acid before a more gradual trend was established. This could possibly be due to the presence of very fine particles in all

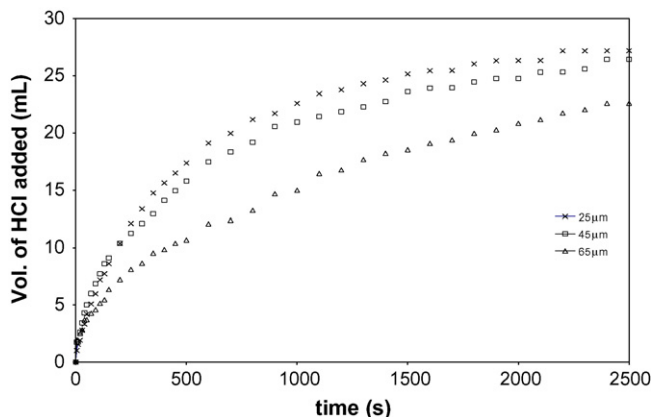


Fig. 2. Effect of particle size on the sorbent conversion as a function of time for sample A.

the samples which react fast with the particles during the initial stages. After these particles have been consumed by the acid solution, the bigger particles will then proceed with the reaction at a gradual rate. Similar results have been reported by Holsten and Gulsun [10].

4.2. Effect of origin

This experiment was carried out to measure the batch, constant pH reactivity of limestone samples obtained from different sources in South Africa. The limestone samples selected had differing chemical and mineralogical compositions. The chemical composition of the different samples used is tabulated in Table 1. All the samples were ground to fine particle size ($-25 \mu\text{m}$). Fig. 3 shows the sorbent conversion vs. time plots for the five samples analyzed. From the results obtained, the GW and LL samples display an initial short region of high dissolution before this settles to a more gradual dissolution rate. This could possibly be due to a higher amount of fine particles in both samples than for the A1 sample. Other than this high initial rate, the samples A1, GW, and LL display an amount of conversion which is comparably close. On the other hand the LD and LYT samples show a lower dissolution rate than the other three. A possible explanation could be found from an examination of their chemical analysis (Table 1). Whereas the A1, GW, and LL samples have a magnesium carbonate content of less than 2 wt.%, the LD and LYT samples have a high content of magnesium carbonate (>35 wt.%).

Previous work by Ahlbeck et al. [8] has associated the presence of Mg with a reduced activity of the sorbent material. Fig. 3 also tends to confirm this observation as sample A which has a lower

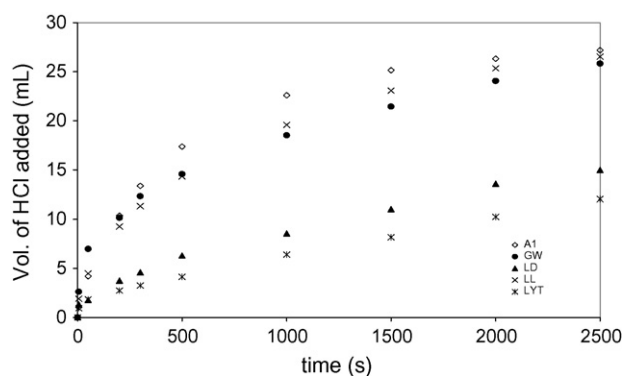


Fig. 3. Conversion vs. time for sorbents from different sources in South Africa.

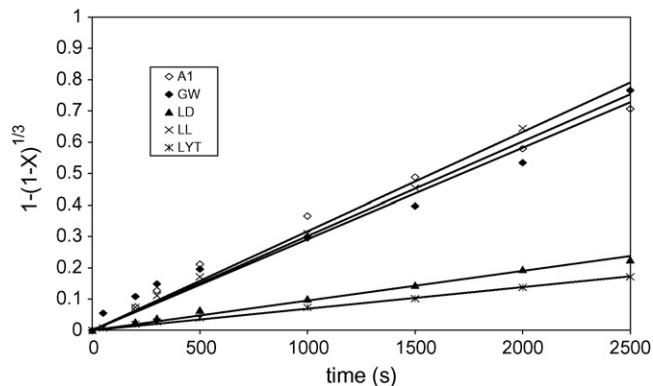


Fig. 4. Plot of $1 - (1 - X)^{1/3}$ vs. time for sorbent dissolution at pH 5.0 and 50 °C.

CaCO₃ content than sample LL nevertheless displays a higher dissolution at any given instant. This could possibly be due to the higher MgCO₃ content of the latter. A comparison of LD and LYT samples also tends to confirm that the source of the sample could as well play an important role in the dissolution rate. LD which has a lower CaCO₃ and a higher MgCO₃ content shows a higher dissolution rate than LYT contrary to expectation.

Fig. 4 shows a plot of $1 - (1 - X)^{1/3}$ vs. time for the five samples used in the study. This result indicates that Eq. (5) is valid for the dissolution of calcium-based materials and that the process is controlled by resistance to chemical reaction. According to Eq. (5), the value of k can be calculated from the slope of the straight lines in Fig. 4. Table 2 shows the values of the reaction rate constants obtained from a consideration of Fig. 4 and Eq. (5).

The information on the effect of origin will be useful to the utility industry to facilitate the acquisition of the best scrubbing agents for FGD systems to be used at existing or planned coal-fired power plants. For example, based on the five samples tested in this study, a utility will choose to utilize the A1 limestone deposit as it is apt to absorb more SO₂ per kilogram of reagent as compared to the other four samples. As transportation costs form a major component of any FGD system, minimizing the amount of sorbent required will result in reduced costs. This is important for the sustainable production of electricity from coal with minimum emissions of SO₂.

4.3. Effect of pH

Five experimental runs were made of sample A, at pH values of 4.0, 4.5, 5.0, 5.5 and 6.0 to try and analyze the effect of the pH on the dissolution rate. Fig. 5 shows the results of the experiments. As can be seen from the results, the dissolution is very fast for the sample dissolved in the pH 4 solution with the dissolution being complete in about 12 min. As the pH is increased, the dissolution rate decreases. For the test carried out at pH 5.0, the dissolution rate is much slower and the process reaches completion after about 90 min. For the test carried out at pH 6.0, the dissolution is not complete even after a test period of 2 h. Previous work by Shih et al. [7] indicated that the dissolution of limestone is controlled by the mass transfer of the hydrogen ions accompanied by chemical

Table 2

Reaction rate constant for the tested sorbents calculated from Eq. (5)

Sample	Constant k (min ⁻¹)
A1	0.0181
GW	0.0175
LD	0.0057
LL	0.0190
LYT	0.00415

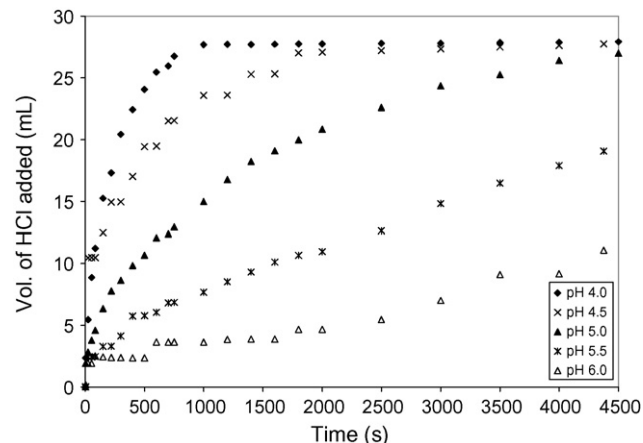


Fig. 5. Influence of the solution pH on the dissolution rate for sample A.

reactions in the mass transfer boundary layer. The reason for the effect of the reaction pH is that increasing the pH increases the apparent mass transfer coefficient.

4.4. Effect of temperature

Experiments were carried out in the 30–70 °C temperature range for sample A1 to investigate the influence of temperature on the dissolution rate. As shown in Fig. 6, increasing the temperature increases the dissolution rate. Fig. 7 shows that the reaction at different temperatures can be modeled using the shrinking core model with surface reaction control. By using the constants derived from the slopes in Fig. 7, the Arrhenius diagram in Fig. 8 was drawn, from which activation energy of 26.1 kJ mol⁻¹ was calculated. There are a wide range of activation energies that have been reported in literature for calcite dissolution; 19 ± 4 kJ mol⁻¹ [17], 21 ± 1 kJ mol⁻¹ [18], 8–60 kJ mol⁻¹ [19]. Gautelier et al. [20] have reported the kinetic study of dolomite dissolution in which the effects of pH (–0.5–5) and temperature (25–80 °C) were investigated. Their values of the activation energy of dolomite dissolution calculated from the Arrhenius plot decreased from 46 to 15 kJ mol⁻¹ as the pH increased from 0 to 5. The relative importance of surface reaction vs. solute transport control of the overall dissolution process depends on temperature and pH. The ratio of the hydrogen ion activity at the surface to the hydrogen ion activity in the solution $a_{H^+, surf}/a_{H^+, bulk}$ is an indication of the reaction controlling mechanism [20]. The closer this ratio is to 1, the more the overall reaction is controlled by the relatively slower rate of surface reaction. At low temperatures

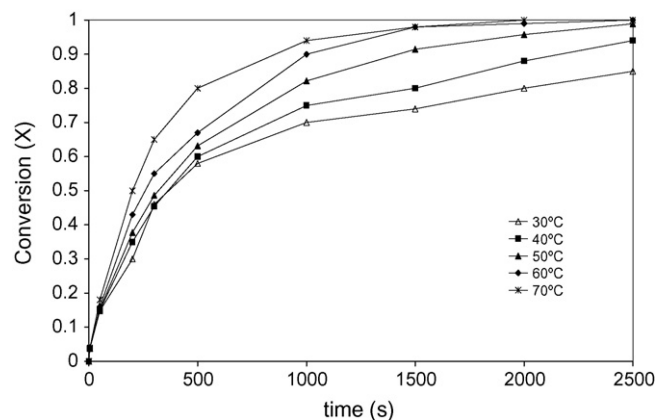


Fig. 6. Effect of temperature on the dissolution rate of sample A1.

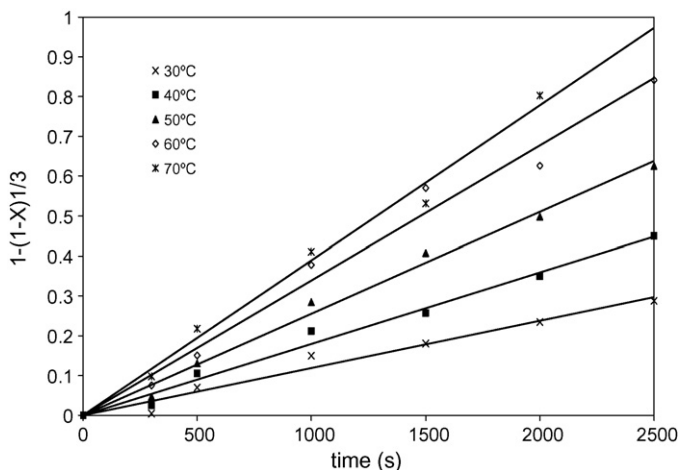


Fig. 7. Plot of $1 - (1 - X)^{1/3}$ vs. time for various reaction temperatures for sample A1.

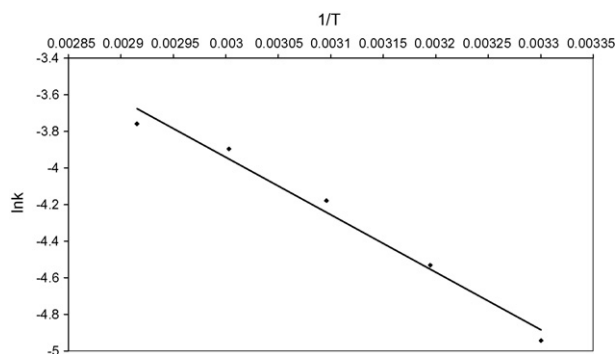


Fig. 8. Arrhenius plot for the dissolution of sample A1.

and pH, Gautelier et al. [20] showed that this ratio is close to 1 but it decreases slightly with increasing temperature and pH, indicating an increasing effect of solute transport on the dissolution rate. It has been generally accepted that a diffusion-controlled process is characterized by being slightly dependent on temperature, while the chemically controlled process is strongly dependent on temperature [21].

5. Conclusions

The dissolution rate of five calcium-based materials from different sources in South Africa was investigated in a pH-Stat apparatus. The study shows that the dissolution rate is a strong function of the particle size; the finer the particle size is, the higher the conversion within the same time period. The dissolution rate was observed to be highly dependent on the solution pH and reactor temperature. From the results, it can be concluded that the pH-Stat method can be used reliably to rank the performance of calcium-based materials as sorbents in the wet flue gas desulphurization process. Based on the five samples tested, sample A is expected to give the best performance while sample LYT shows the poorest. Kinetic analysis of

the dissolution rate shows that the process can be modeled using the shrinking core model with surface control. The value of the apparent activation energy obtained for sample A (26.1 kJ mol^{-1}) compares favorably with those reported in literature.

Acknowledgements

The authors acknowledge the financial assistance of Tshwane University of Technology, Germany Academic Exchange service (DAAD), Eskom-South Africa and NRF-THRIP funding (TP 2005102400018).

References

- [1] S.-F. Randall, D.K. Matibe, Electricity and externalities in South Africa, *Energy Policy* 31 (2003) 721–734.
- [2] J. Kaminski, Technologies and costs of SO_2 -emissions reduction for the energy sector, *Applied Energy* 75 (2003) 165–172.
- [3] R.V. Bravo, C.F. Camacho, V.M. Moya, A.I. Garcia, Desulphurization of SO_2 - NO_2 mixtures by limestone slurry, *Chemical Engineering Science* 57 (2002) 2047–2058.
- [4] L. Eisenlohr, K. Meteva, F. Gabrovsek, W. Dreybrodt, The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous H_2O - CO_2 solutions, *Geochimica et Cosmochimica Acta* 63 (1999) 989–1002.
- [5] Z. Liu, W. Dreybrodt, Dissolution kinetics of calcium carbonate minerals in H_2O - CO_2 solutions in turbulent flow: the role of the diffusion boundary layer and the slow reaction $\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$, *Geochimica et Cosmochimica Acta* 61 (1997) 2879–2889.
- [6] L. Plan, Factors controlling carbonate dissolution rates quantified in a field test in the Austrian Alps, *Geomorphology* 68 (2005) 201–212.
- [7] S.-M. Shih, J.-P. Lin, G.-Y. Shiau, Dissolution rates of limestones of different sources, *Journal of Hazardous Materials B79* (2000) 159–171.
- [8] J. Ahlbeck, T. Engman, S. Falten, M. Vihma, Measuring the reactivity of limestone for wet flue gas desulphurization, *Chemical Engineering Science* 50 (1995) 1081–1089.
- [9] P. Fellner, V. Khandl, Characterization of limestone reactivity for absorption of SO_2 from Fume gases, *Chemical Papers* 53 (1999) 238–241.
- [10] C. Hosten, M. Gulsun, Reactivity of limestone from different sources in Turkey, *Minerals Engineering* 17 (2004) 97–99.
- [11] J.B.W. Frandsen, S. Kiil, J.E. Johnsson, Optimisation of a wet FGD pilot plant using fine limestone and organic acids, *Chemical Engineering Science* 56 (2001) 3275–3287.
- [12] Clean Coal Technology: Advanced technologies for the control of sulphur dioxide emissions from coal-fired boilers, Technical Report Number 12, 1999.
- [13] D.L. Hammack, W.F. Gohara, Use of stack emissions to control DBA enhanced FGD systems burning fuel highly variable in sulfur content, in: EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium, BR-1641, August 25–29, 1997.
- [14] T. Takashina, S. Honjo, N. Ukawa, K. Iwashita, Effect of Ammonium Concentration on SO_2 Absorption in a Wet Limestone Gypsum FGD Process, 35, The Society of Chemical Engineers, Japan, 2002, pp. 197–204.
- [15] O. Levenspiel, *Chemical Reaction Engineering*, second ed., New York, 1972.
- [16] J. Cama, C. Ayora, A. Lasaga, The deviation from equilibrium effect on dissolution rate and on apparent deviations in activation energy, *Geochimica et Cosmochimica Acta* 63 (1999) 2481–2486.
- [17] M. Alkattan, E.H. Oelkers, J.-L. Dandurand, J. Schott, An experimental study of calcite and limestone dissolution rates as a function of pH from -1 to 3 and temperature from 25 to 80 °C, *Chemical Geology* 151 (1998) 199–214.
- [18] D.K. Gledhill, J.W. Morse, Calcite dissolution kinetics in Na-Ca-Mg-Cl brines, *Geochimica et Cosmochimica Acta* 70 (2006) 5802–5813.
- [19] J.W. Morse, R.S. Arvidson, The dissolution kinetics of major sedimentary carbonate minerals, *Earth Science Reviews* 58 (2002) 51–84.
- [20] M. Gautelier, E.H. Oelkers, J. Schott, An experimental study of dolomite dissolution rates as a function of pH from -0.5 – 5 and temperature from 25 to 80 °C, *Chemical Geology* 157 (1999) 13–26.
- [21] S. Aydogan, M. Erdemoğlu, G. Uçar, A. Aras, Kinetics of Galena dissolution in nitric acid solutions with hydrogen peroxide, *Hydrometallurgy* 88 (2007) 52–57.