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THE DISSOLUTION STUDY OF A SOUTH AFRICAN MAGNESIUM-BASED MATERIAL FROM DIFFERENT SOURCES USING A pH-STAT

One of the main steps in the wet flue gas desulphurization (WFGD) process is the dissolution of either magnesite or limestone. Evaluating the magnesite dissolution rate is vital for the design and efficient operation of wet FGD plants. A study on the dissolution of magnesite from different sources in South Africa is presented in this work. The effect of reaction temperature (303.15–343.15 K), solid-to-liquid ratio (0.5–2.5g/200 ml), particle size (25–125 μm), pH (4–6) and HCl concentration (0.5–2.5 mol/l) on the dissolution rate was studied. It was found that the dissolution reaction follows a shrinking-core model with the chemical reaction control as the rate-controlling step. The dissolution rate increased with an increase in concentration and reaction temperature and with a decrease in particle size and solid-to-liquid ratio. The activation energy of this dissolution process was found to be 45.685 kJ/mol.

Keywords: desulphurization; dissolution; ammonium compounds; pH-Stat.

Sulphur dioxide (SO_x) and nitrogen oxides (NO_x) are both major causes of acid rain, and are both emitted from stationary combustion facilities such as power plants, incinerators and combustors. Therefore, there is a need to remove the above mentioned oxides so as to protect the atmosphere against pollution.

WFGD is the most common process used in thermal power station to remove sulphur dioxide from coal [1,2]. In this process, either calcium based (limestone) or magnesium-based material (magnesite or dolomite) is dissolved into absorption slurry tank. Ca²⁺ and Mg²⁺ react with sulphur dioxide to form solid product of CaSO₄ or MgSO₄, respectively [3].

The dissolution kinetics of calcium or magnesium based compound are very crucial in wet flue gas desulphurisation [4–6]. Several studies have focused on dissolution rates of magnesite mineral. Abali *et al.* [7] investigated the dissolution of magnesite mineral in aqueous sulphur dioxide and they found that the

dissolution is controlled by surface reaction. Raschman [8] studied leaching of calcined magnesite using ammonium chloride at constant pH. The study showed that the leaching process is controlled by the chemical reaction of MgO with H⁺ at the liquid-solid interface and by pore diffusion.

Saldi *et al.* [9] investigated magnesite dissolution rate at neutral to alkaline conditions and 150 and 200 °C as function of pH, total dissolved carbonate concentration, and chemical affinity, they found that the dissolution rate increases with increasing ionic strength, but decrease with increasing temperature from 150 and 200 °C, pH, and aqueous CO₃²⁻ activity. The measured rates were interpreted using the surface complexation model developed by Pokrovsky *et al.* [10] in combination with transition theory [11].

Demir *et al.* [12] investigated the dissolution kinetics of magnesite when leached with citric acid solutions and observed that chemical reaction controls the dissolution rate. Fedorockova *et al.* [13] studied the inhibiting effect of HCl solution on the dissolution rate of magnesium oxide during the leaching of dead-burnt magnesite. The study concluded that dissolution of MgO is controlled by chemical reaction. The effect of acetic acid solution in the dissolution of magnesite in acetic acid solutions has been studied by La-

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çin *et al.* [14] it was established that the dissolution rate was controlled by chemical reaction. According to the work carried out by Bakan *et al.* [15], the dissolution kinetics of natural magnesite in lactic acid solutions is controlled by surface chemical reaction. Zafar [16] investigated the dissolution of bauxite ore with sulphuric using a semi empirical kinetic model and established that the dissolution was controlled by the shrinking core model.

The main objective of this study is to determine the feasibility of using South African magnesite to produce absorbent for flue gas desulphurization, especially in regions where limestone is scarce. Five magnesium-based materials from different sources in South Africa are investigated using a pH-Stat apparatus. The effect of experimental parameters including the HCl concentration, reaction temperature, solid-to-liquid ratio, particle size and pH on dissolution rate of magnesite from South Africa was investigated. A semi empirical kinetic expression model is developed based on the shrinking core model.

MATERIAL AND METHODS

Materials

Five types of natural magnesite used were obtained from different mines and their outskirts in South

Africa, this are: MG1 (Atlas mine, Mpumalanga province), MG2 (Folovhodwe mine, Limpopo province), MG3 (Strathmore mine, Mpumalanga province), MG4 (outskirts of Atlas mine), and MG5 (outskirts of Folovhodwe mine).

The raw samples were cleaned, crushed, ground and sieved at different particle sizes. Chemical analysis of the magnesite used is shown in Table 1.

Methods

In the first step, batch dissolution of magnesite from different sources were carried out at a constant temperature, concentration of HCl solution, solid-to-liquid ratio, particle size, stirring speed and pH of 323.15 K, 1.00 mol/L, 1.50/200 g/mL, 50 μ m, 200 rpm and 5, respectively. Batch dissolution rates for MG3 magnesite were varied with the process variables (temperature, pH, HCl concentration, solid-to-liquid ratio and particle size) and were measured using a pH-Stat apparatus at a stirring speed of 200 rpm. The pH-Stat apparatus is shown in Figure 1. The factors that were expected to affect the dissolution rate were chosen the range of parameters are given in Table 2.

Table 1. Chemical analysis of magnesite from different sources

Component	MG1	MG2	MG3	MG4	MG5
Al ₂ O ₃	3.85	3.58	1.84	5.95	4.48
SiO ₂	1.83	3.53	1.61	1.52	4.36
Fe ₂ O ₃	1.93	2.33	1.31	1.83	1.67
MgCO ₃	89.21	82.39	93.1	68.39	63.54
CaCO ₃	3.18	8.17	2.14	22.31	25.95
Ignition loss	36.6	46.6	13.21	35.6	13.41

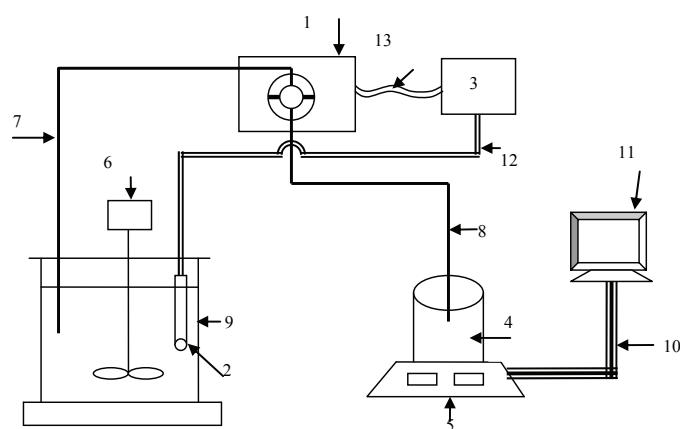


Figure 1. A schematic drawing of the experimental set-up. 1) Peristaltic pump, 2) pH electrode, 3) pH controller, 4) acid solution beaker, 5) electronic balance, 6) stirrer, 7,8) plastic tubing, 9) reaction vessel, 10) cable, 11) computer work station, 12) wiring for pH electrode, 13) connection between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

Table 2. The ranges of parameters used on the experiment

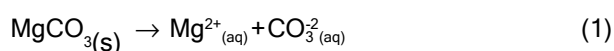
Parameter	Values				
Concentration, mol/L	0.5	1 ^a	1.5	2.0	2.5
Particle size, μm	25	50 ^a	75	100	125
Temperature, K	303.15	313.15	323.15 ^a	333.15	343.15
pH	4	4.5	5 ^a	5.5	6
Solid/liquid ratio, g/mL	0.5/200	1.0/200	1.5/200 ^a	2.0/200	2.5/200

^aThe process parameters that were held constant to determine the effect of process parameters on the dissolution of magnesite

RESULTS AND DISCUSSION

Effect of adding HCl solution

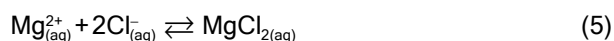
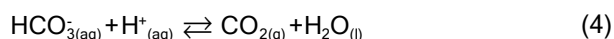
Magnesite is insoluble in water and partially ionizes according to the following equation:



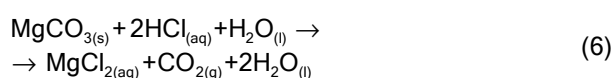
HCl is a strong acid and it ionizes according to the following reaction:



The CO_3^{2-} reacts with hydrogen to form HCO_3^- (aq), and the HCO_3^- (aq) further reacts with hydrogen to form carbon dioxide and water. This is shown by reactions (3) and (4), respectively.



Reaction (5) is negligible. The overall reaction during the dissolution process when magnesite is dissolved in HCl solution is as follows:



More magnesite dissolves because the carbonate is consumed by reaction (3). Reaction (3) is very fast, and more Mg^{2+} is also consumed by reaction (5) shifting the equilibrium to the right [17].

Effects of using magnesite from different sources

From Table 1, the samples chosen from different areas have different chemical compositions. Figure 2 shows the conversion vs. time plots for the five samples analyzed. From the results, MG3 magnesite had a higher dissolution rate followed by MG1 magnesite. This could be explained from the chemical composition. MG3 and MG1 have greater amount of magnesium carbonate compared to MG5, MG2 and MG4 magnesite. Previous work [18] shows that the calcium ions can get absorbed into the magnesite surface and thus this inhibits the dissolution.

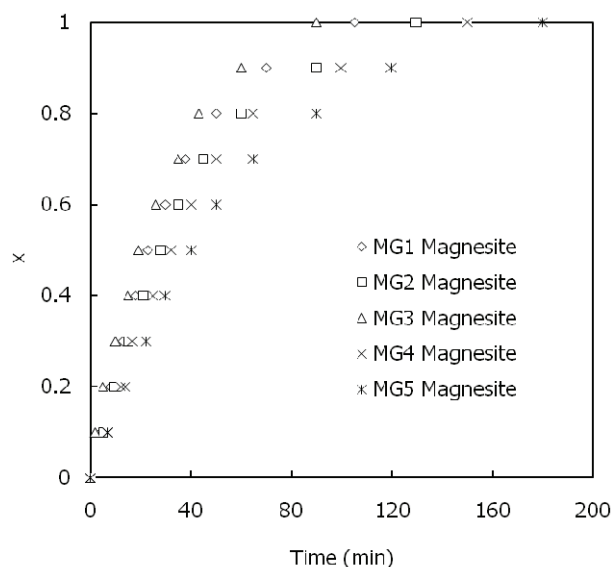


Figure 2. Conversion vs. time plots for the five magnesite samples used in the study.

Figure 3 shows a plot of $1-(1-X)^{1/3}$ vs. time for the five samples used in the study. This result indicates the dissolution of magnesite is controlled by a chemical reaction. Using Eq. (9), the value of rate constant can be calculated from the slope of the straight lines in Figure 3. Table 3 presents the values of the reaction rate constants. Analyzing the dissolution of magnesite from different sources, the most suitable magnesite that can be used as a sorbent in wet flue gas desulphurization is selected.

Based on the five samples tested, MG3 magnesite can be used effectively in wet flue gas desulphurization process compared to the other four samples. This will reduce transportation costs of limestone to places where magnesite is abundant.

Effect of reaction parameters

Effect of concentration

To study the effect of the HCl concentration on the dissolution rate, the experiments were carried out in the 0.5–2.5 mol/L concentration range while the temperature, particle size, stirring speed, pH and solid-to-liquid ratio were kept constant at 323.15 K, 50

μm, 200 rpm, 5 and 1.5/200 g/mL, respectively. The results show that the dissolution rate increases with an increase in solution concentration (Figure 4a).

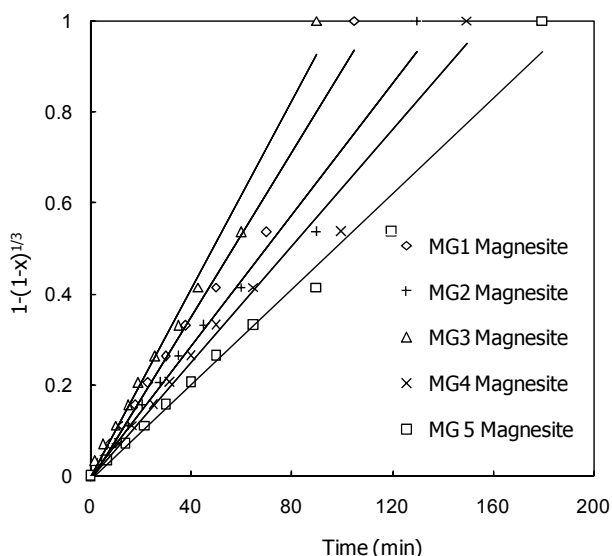


Figure 3. Plot of $1-(1-X)^{1/3}$ vs. time for the five samples used in the study.

Table 3. Rate constants of magnesite from different sources

Type of magnesite	Rate constant, min ⁻¹
MG1	0.009
MG2	0.007
MG3	0.012
MG4	0.0061
MG5	0.0050

Effect of particle size

The dissolution rate was studied using magnesite of particle size between 25-125 μm. The solid-to-liquid ratio, concentration of HCl, stirring speed and reaction temperature were kept constant at 1.5/200 g/mL, 1.00 mol/L, 200 rpm and 323.15 K, respectively. Results of the effect of particle size are presented in Figure 4c. As shown in Figure 4b, as the particle size decreases, the dissolution rate increases.

Effect of reaction temperature

To study the effect of reaction temperature on the dissolution rate, four different reaction temperatures were varied in the range of 303.15-343.15 K. The concentration of the solution, solid-to-liquid ratio, particle size and stirring speed were kept constant at 1.00 mol/L, 1.50/200 g/mL, 45 μm and 200 rpm respectively. The experimental results are shown in Figure 4c, it can be seen that the dissolution rate increases as the reaction temperature increases.

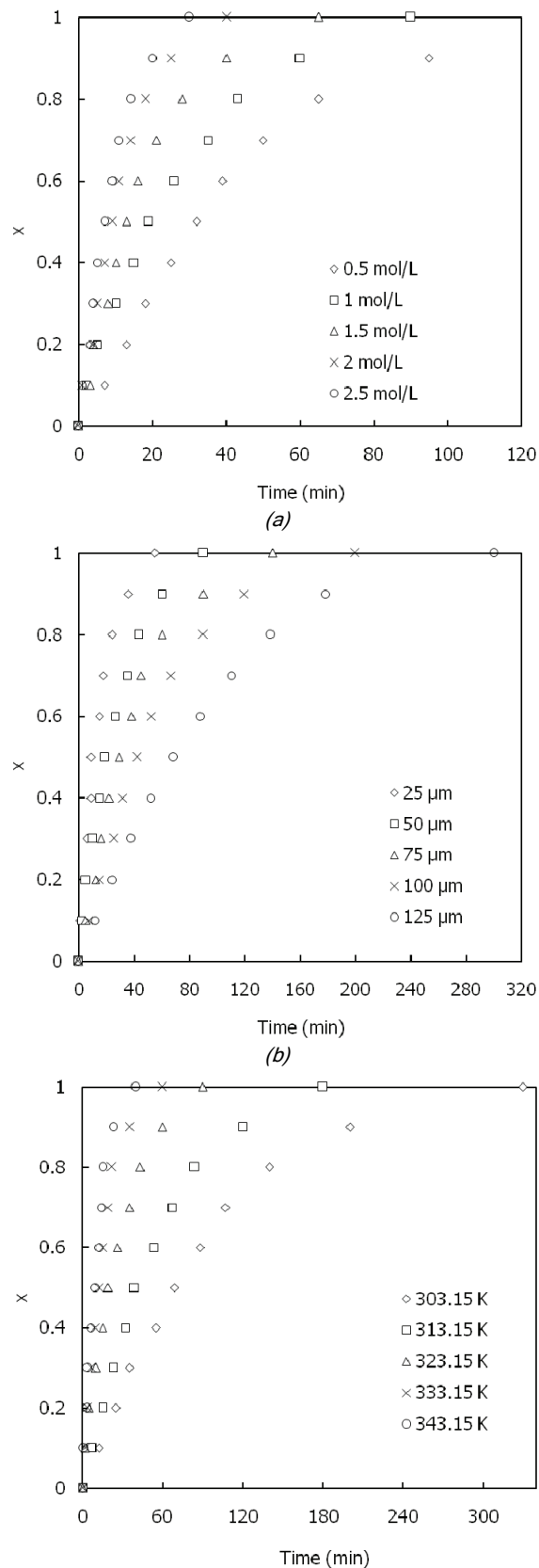
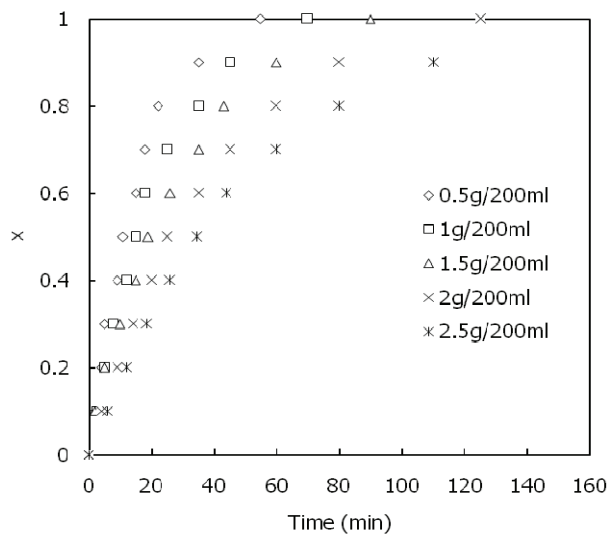
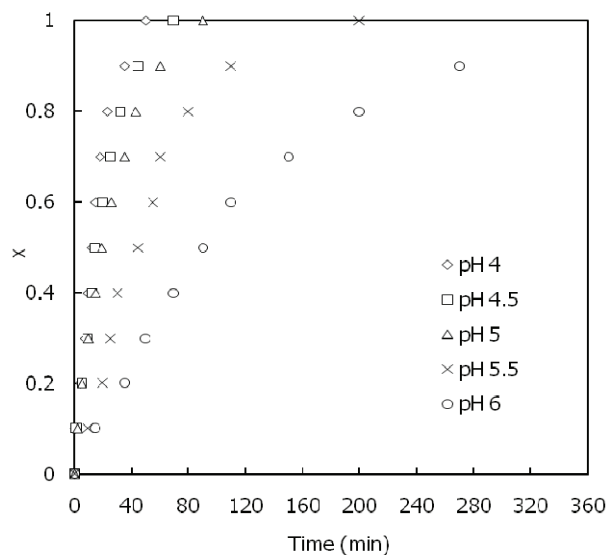


Figure 4. Conversion vs. time plots for different: a) concentration; b) particle size; c) reaction temperature.



(d)



(e)

Figure 4. (Continued) Conversion vs. time plots for different: (d) solid to liquid ratio and (e) pH.

Effect of solid-to-liquid ratio

To determine the effect of solid-to- liquid ratio on the dissolution rate, experiments were performed with four different solid-to-liquid ratios in the range of 0.5/200-2.5/200 g/ml. The reaction temperature, concentration of solution, particle size, solid-to-liquid ratio and stirring speed were kept constant at 323.15 K, 1.00 mol/L, 50 μm, 1.50/200 g/mL and 200 rpm, respectively. From Figure 4d, it can be seen that the dissolution rate decreases as the solid-to-liquid ratio increases. This is because when lesser amount of magnesite is used; there will be more H⁺ for dissolution and *vice versa*.

Effect of pH

To determine the effect of pH on the dissolution rate, the experiments were performed at five different pH values in the range of 4-6. Keeping the reaction temperature, concentration of solution, particle size, solid-to-liquid ratio and stirring speed were kept constant at 323.15 K, 1.00 mol/L, 50 μm, 1.50/200 g/mL and 200 rpm, respectively. The results are presented in Figure 4e.

At low pH (4 and 5) the dissolution rate is very fast - this means it is directly proportional to hydrogen concentration. At pH above 5, the dissolution rate is slow. Previous work [19] shows that the reaction could be controlled by diffusion of OH⁻, HCO₃⁻ and other species and by the finite rate of CO₂ reaction.

Kinetics analysis

In order to determine the kinetic parameters and the rate-controlling step for the dissolution of magnesite, the experimental data were analyzed using the shrinking core model (SCM). From the shrinking core model, the reaction is considered to take place first at the outer surface of the particle [20]. The region of the reaction goes into the solid and the reacting particle shrinks during the reaction. The following three steps are considered to occur in series during the reaction:

1. Diffusion of the fluid reactant from the main body of the fluid film to the surface of the solid.
2. Reaction on the surface between the fluid reactant and the solid.
3. Diffusion of the fluid reactant to the surface of the unreacted core.

The rate of a non-catalytic heterogeneous reaction is generally controlled by either of the following steps: diffusion through the product layer or the fluid film or the chemical reaction at the surface of the core of the unreacted particle. From these steps, the rate equations can be integrated and can be written as follows:

$$X = \frac{3bk_g C_A}{\rho_B R_0} t = k_r t \quad (\text{The film diffusion control}) \quad (7)$$

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = \frac{6bD_e C_A}{\rho_B R_0^2} t = k_d t \quad (8)$$

(The product layer diffusion)

$$1 - (1 - X)^{1/3} = \frac{bk_s C_A}{\rho_B R_0} = k_r t \quad (9)$$

(The chemical reaction control)

The apparent dissolution rates constant and their correlation were calculated from the experimental data using Eqs. (8) and (9). This is shown in Table 4. In accordance with this result, the equation representing

the kinetics of this process was determined to obey the chemical reaction model. This is because according to Table 4, the largest regression coefficient was obtained for the chemical reaction model. The effects of concentration, particle size, temperature, solid-liquid ratio and pH on the dissolution rate constant are shown in Figures 5a-5e, respectively. The results obtained from calculating the rates constant are in excellent agreement with result obtained from dissolution rate.

A semi empirical model which includes the effects of the reaction parameters on the rate constant of reaction can be derived as follows:

$$k_r = k_0 C^a D^b \left(\frac{S}{L}\right)^c P^d e^{-E_a/RT} \quad (10)$$

Combining Eqs. (9) and (10), the following equation is obtained:

$$1-(1-X)^{1/3} = k_0 C^a D^b \left(\frac{S}{L}\right)^c P^d e^{-E_a/RT} t \quad (11)$$

The constants a , b , c and d were estimated from the apparent rate constants given in Table 4.

To determine the reaction order a plot of $\ln k_r$ versus $\ln C$ was drawn in Figure 6 using the data in

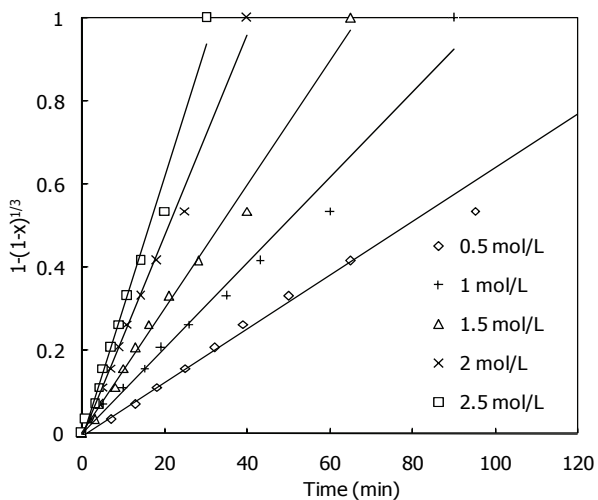
Table 4. The gradient of the straight line is the reaction order with respect to concentration. The reaction order is proportional to 0.975 power of concentration with a correlation coefficient of 0.966. The particle size, solid-to-liquid ratio and pH reaction order was found to be proportional to power of -0.871, -1.192 and -0.166 to the particle size, solid-to-liquid ratio and pH, respectively. The correlation coefficients of these parameters are 0.950, 0.839 and 0.859, respectively. This can be seen in Figures 7-9, respectively.

The Arrhenius equation was used to calculate activation energy of the dissolution process. The Arrhenius plot is shown in Figure 10. From the gradient of the straight line, the activation energy was calculated to be 45.685 kJ/mol. The intercept was determined to be 11.07. For chemical controlled process, the activation energy is usually greater than 40 kJ/mol [21]. This shows that the dissolution of magnesite in HCl is controlled by surface chemical reaction. Thus, eq. (11) yields:

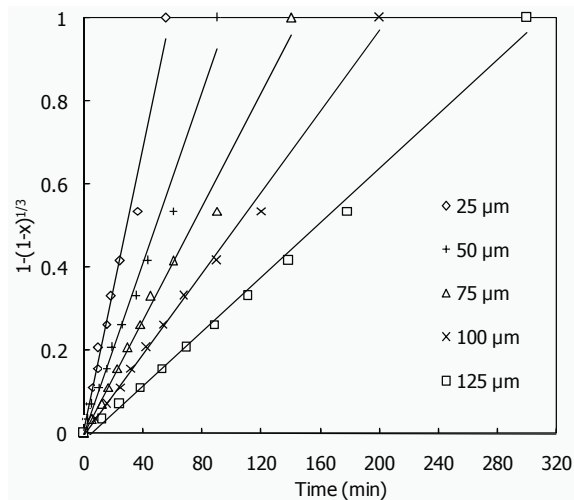
$$1-(1-X)^{1/3} = 11.07 C^{0.975} D^{-0.871} \left(\frac{S}{L}\right)^{-1.192} P^{-0.166} e^{-45685/RT} t$$

Table 4. K_r and K_d correlation coefficients values

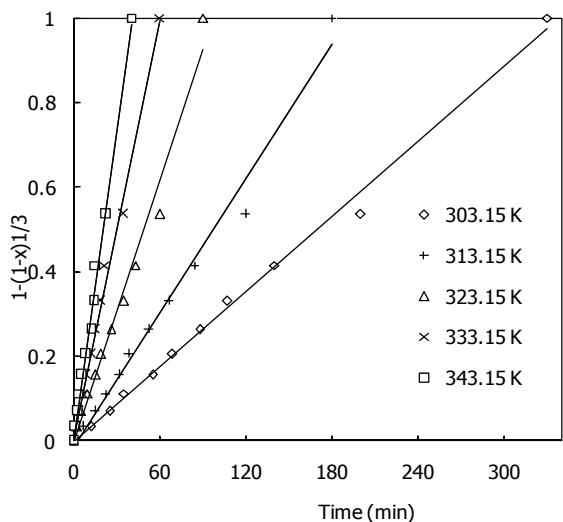
Parameter	Surface chemical reaction: $1-(1-X)^{1/3}$		Diffusion rate through a product layer: $1-3(1-X)^{2/3}+2(1-X)$	
	K_r / min^{-1}	R^2	K_d / min^{-1}	R^2
Concentration, mol/L				
0.5	0.0060	0.991	0.0058	0.987
1	0.0120	0.982	0.0130	0.974
1.5	0.0140	0.992	0.0158	0.990
2	0.0240	0.992	0.0250	0.981
2.5	0.0310	0.985	0.0330	0.976
Particle size, μm				
25	0.0170	0.984	0.0180	0.979
50	0.0120	0.992	0.0130	0.964
75	0.0061	0.985	0.0068	0.986
100	0.0042	0.992	0.0050	0.974
125	0.0031	0.995	0.0028	0.964
Solid-to-liquid ratio, g/mL				
0.5/200	0.0170	0.989	0.0180	0.982
1/200	0.0130	0.986	0.0140	0.981
1.5/200	0.0120	0.982	0.0130	0.974
2/200	0.0071	0.988	0.0081	0.982
2.5/200	0.0051	0.987	0.0049	0.984
Temperature, K				
303.15	0.0031	0.995	0.0029	0.988
313.15	0.0051	0.985	0.0051	0.977
323.15	0.0120	0.982	0.0130	0.974
333.15	0.0163	0.994	0.0170	0.987
343.15	0.0242	0.993	0.0260	0.977



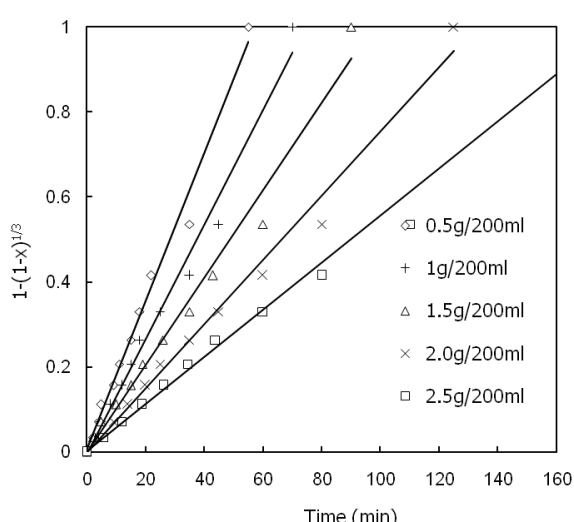
(a)



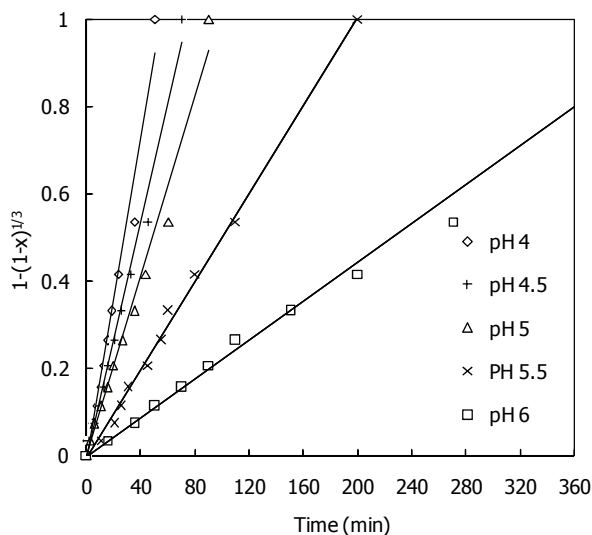
(b)



(c)



(d)



(e)

Figure 5. Variation of $1-(1-X)^{1/3}$ versus time for different: a) concentration, b) particle size, c) reaction temperature, d) solid to liquid ratio and e) pH.

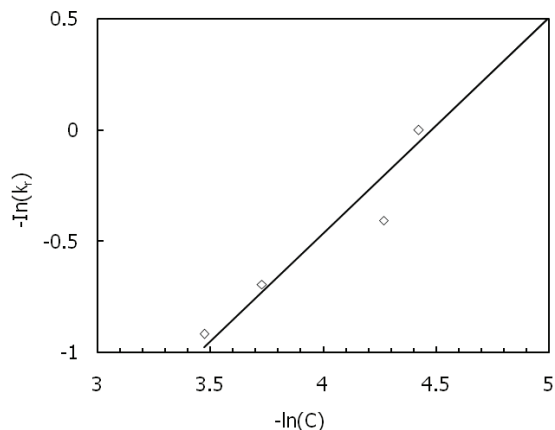


Figure 6. Plot of $\ln k_r$ vs. $\ln C$.

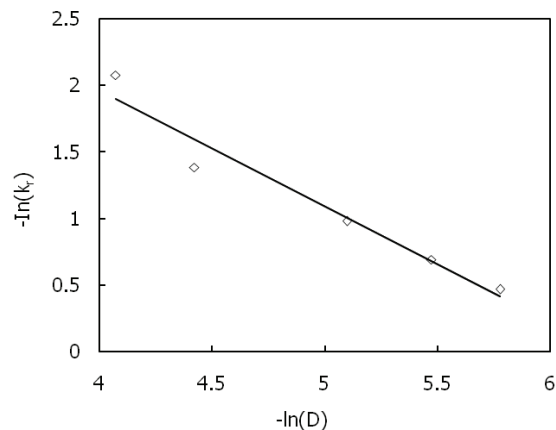


Figure 7. Plot of $\ln k_r$ vs. $\ln D$.

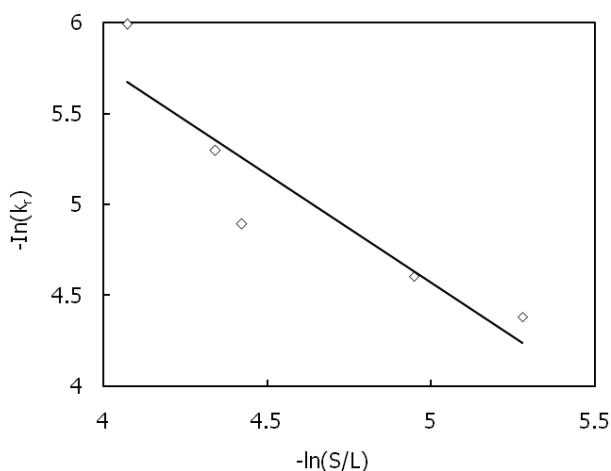


Figure 8. Plot of $\ln k_r$ vs. $\ln(S/L)$.

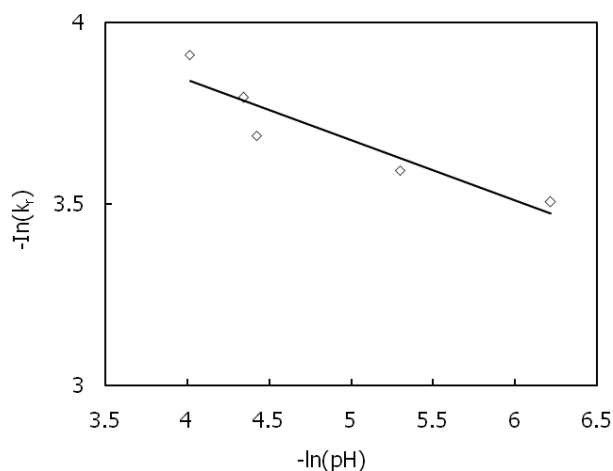


Figure 9. Plot of $\ln k_r$ vs. $\ln pH$.

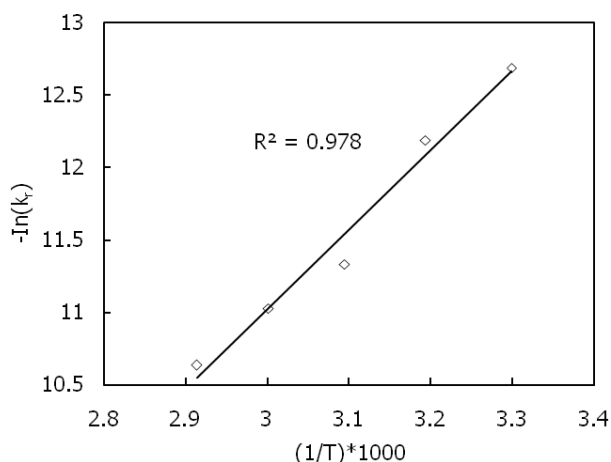


Figure 10. Arrhenius plot for the dissolution rate (k_r) of the magnesite based material in HCl solution.

CONCLUSIONS

In this study, the dissolution rate of magnesite from different sources was investigated. The effects of the chosen parameters on the dissolution rate were examined and evaluated. It was determined that the

conversion rate increased with an increase in HCl concentration and reaction temperature and with a decrease in solid-to-liquid ratio and particle size. The apparent activation energy obtained for MG3 magnesite was 45.685 kJ/kmol. This indicated that the dis-

solution kinetics follows a shrinking-core model with the chemical reaction control as the rate-controlling step. Based on the five samples tested, sample MG3 offered the best dissolution rate constant. This means it can be used effectively as a sorbent in wet flue gas desulphurisation.

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Notations

a, b, c, d	Power constants in Eq. (11)
C	Concentration of acetic acid (mol/L)
C_A	Bulk concentration of the fluid (mol/cm ³)
D	Particle diameter (cm)
De	Effective diffusion coefficient (cm ² /s)
E_a	Activation energy (J/mol)
k_d	Apparent rate constant for diffusion through the product layer (s ⁻¹)
k_g	Mass-transfer coefficient for the fluid film (cm/s)
k_f	Apparent rate constant for the surface chemical reaction (s ⁻¹)
k_s	Rate constant of surface reaction (cm/s)
k_0	Frequency or pre-exponential factor (s ⁻¹)
K_1	Apparent rate constant for diffusion through fluid films
P	pH
S/L	Solid-to-liquid ratio (g/mL)
R	Universal gas constant (J/mol K)
R_0	Average radius of solid particle (cm)
t	Reaction time (s)
T	Temperature (K)
X	Converted fraction
ρ_B	Molar density of solid reactant (mol/cm ³)

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NAUČNI RAD

ISPITIVANJE RASTVARANJA JUŽNOAFRIČKOG MATERIJALA NA BAZI MAGNEZIJUMA IZ RAZLIČITIH IZVORA PRI KONSTANTNOJ pH VREDNOSTI

Jedan od glavnih koraka u mokrom odsumporavanju dimnih gasova (MODG) je proces rastvaranja magnezita ili krečnjaka. Određivanje brzine rastvaranja magnezita je od vitalnog značaja za projektovanje i efikasan rad postrojenja za MODG. U ovom radu su prezentovani rezultati vezani za ispitivanje rastvaranja magnezita iz različitih izvora u Južnoj Africi. Proučavan je uticaj reakcione temperature (303, 15-343, 15 K), odnosa čvrsto-tečno (0,5-2,5 g/200 ml), veličine čestica (25-125 μm), pH vrednosti (4-6) i koncentracije HCl (0,5-2,5 mol/l) na brzinu rastvaranje. Utvrđeno je da reakcija rastvaranja prati model neizreagovanog jezgra, sa hemijskom reakcijom kao stupanjem koji kontrolise brzinu procesa. Brzina rastvaranja se povećava sa povećanjem koncentracije i reakcione temperature, i sa smanjenjem veličine čestica i odnosom čvrsto-tečno. Utvrđena je i vrednost aktivacione energije koja iznosi 45,685 kJ/mol.

Ključne reči: desulfurizacija; rastvaranje; amonijum jedinjenja, pH.