KINETIC STUDY OF REACTION BETWEEN DOLOMITE ORE AND TRIOXONITRATE (V) ACID (HNO$_3$)

Comfort Temitope ARE [1,2], *Mohammed Abubakar Tanko SULEIMAN*[1], *Jonathan YISA*[1],
Manase AUTA[3]*, Isaac Adekunle JOSEPH*[3]

1 *Federal University of Technology, Chemistry Department, Minna, Niger State, Nigeria*
2 *Prince Abubakar Audu University, Chemistry Department, Anyigba, Kogi State, Nigeria*
3 *Federal University of Technology, Chemical Engineering Department, Minna, Niger State, Nigeria*
E-mail: josephcomfort110818@yahoo.com

ABSTRACT

The leaching of dolomite (carbonate mineral of calcium and magnesium) in mineral acid such as HNO$_3$ is environmentally friendly with low energy demands, and it has high capacity of processing both in low and high grade ore. The study of the reaction kinetics and mechanism of reaction between dolomite and HNO3 was investigated. The energy-dispersive X-ray spectroscopy (EDS) result showed that Ikpeshi dolomite ore consists of calcium (20.09 %), magnesium (13.93 %) and oxygen (65.99 %). The effect of HNO$_3$ concentration between 0.5 and 2.5 M on the fraction of dolomite was studied, while the reaction temperature was between 30 and 70 °C; the reaction time was 20 to 60 min. The results show the fraction of dolomite that reacted in HNO3 increased as the temperature and concentration increased. Reacted fraction of 0.995 was achieved at 50 min reaction time, acid concentration of 2.5 M, agitation speed of 250 revolution per minutes (rpm) and reaction temperature of 55 °C. The reaction mechanism followed product layer diffusion control of $1+2(1–x) – 3(1–x)^{2/3} = kt$ with 0.915 reaction order of hydrogen ion concentration and activation energy of 26.6 KJmol^{-1}.

Keywords: Activation energy; Product layer diffusion control; Reacted fraction; Reaction kinetic.

1   INTRODUCTION

Extractive metallurgy often employs the leaching technics in the recovery of valuable components from solid mineral ores in aqueous solutions. This method is applied in hydrometallurgical processes due to its low negative environmental impact, low energy consumption, and its efficient recovery of low grade ore [1,2,3]. Dolomite is a double carbonate mineral of calcium and magnesium with the chemical formula CaMg(CO$_3$)$_2$ and it is commonly found in marine and continental rocks [4,5]. Variations in the colour of dolomite can be linked to the presence of the impurities in it. Some dolomite appears as green, pink, brown, white and black [6,7,8]. Pink dolomite sample was collected for this study from Ikpeshi mines in Edo State. Dolomite is one of the major sources of magnesium oxide (MgO) which is currently in high demand [9,10]. MgO can be used as catalyst, refractory lining, in drug making and fertilizer production [11,12]. In order to understand the reaction mechanism between dolomite and mineral acids, such as hydrochloric acid (HCl), tetraoxosulphate (VI) acid (H$_2$SO$_4$) and trioxonitrate (V) acid (HNO$_3$), the study of dissolution kinetics was considered.

Baba et al. [1] studied the dissolution kinetics of dolomite from Oreke Village, Felodun Local Government Area of Kwara State in HCl. 0.993 leaching fraction was attained at temperature of 80 °C, 60 min and acid concentration of 2 M. The study also established that the kinetics followed ash layer diffusion control mechanisms, half reaction order with hydrogen ion and 20.77 KJ/mol activation energy. Pultar et al. [13] studied the effect of acid concentration on the reaction of dolomite with nitric acid using Sherwood criterion equation and reported leaching fraction of 0.8 at 25 hours, temperature of 40 °C and acid concentration of 0.1 M. The effect of temperature showed a little above 0.8 leaching fraction at temperature of 60 °C, 16 hours and acid concentration of 0.05 M. Further study is necessary on the leaching of dolomite in HNO_3 due to the limited reports. The prolongued leaching time and low leaching efficiency of dolomite in HNO_3 reported by Pultar et al. [13] might not be economical in real industrial application as the leaching equipment will be overstretched with high energy consumption and delay in production process. Therefore, this research is aimed at studying the reaction kinetics of dolomite in HNO_3 using the shrinking core model (SKM) in order to improve the reaction time and the reaction kinetics.

2 MATERIAL AND METHODS

2.1 Chemicals and materials

Dolomite ore sample was sourced from Ikpeshi mines in Edo State of Nigeria. The sample was ground and sieved into particle size between 0.15 and 0.3 mm before EDS analysis. HNO_3 (analytical grade, 70 %) was purchased from Panlac chemical shop, Minna, Niger state, Nigeria.

2.2 Kinetic study

The reaction was carried out in a 250 mL conical flask using 3 g of the ore sample. 100 mL of the HNO_3 solution was measured into the reactor at each experimental run. Effect of concentration on the fraction of dolomite that reacted was studied between 0.5 and 2.5 M while the temperature was kept constant at 55 °C based on the preliminary experiment. The agitation speed was fixed at 200 rpm [1], each of the acid concentration was studied between 20 to 60 min leaching time. After each leaching process, the reactor content was immediately poured into funnel containing 11 CM Whatman filter paper in order to prevent further leaching. The fraction of dolomite that reacted was calculated using Equation (1). The above procedures were repeated for the study of the effect of temperature between 30 and 70 °C on the leaching fraction. The kinetics plots were obtained from the experimental data. The experimental setup is shown in Figures 1 to 5 below.

$$Leaching\ fraction = \frac{Mass\ of\ dissolved\ dolomite}{Initial\ mass\ of\ dolomite} \tag{1}$$

Figure 1: *Dolomite stone*

Figure 2: *Sieved dolomite sample*

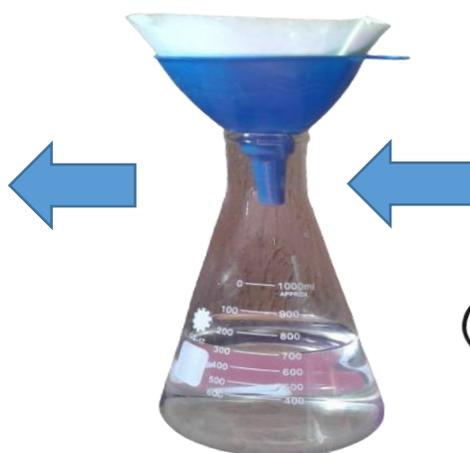**Figure 3.** Residue   **Figure 4.** Filtration   **Figure 5.** Dissolution of dolomite in HNO$_3$

3 RESULT AND DISCUSSION

3.1 Characterization of dolomite

The energy-dispersive X-ray spectroscopy (EDS) result presented in Fig. 6 shows the peaks of the three major elemental compositions of dolomite. Table 1 shows the percentage composition of the dolomite ore: calcium (20.09 %), magnesium (13.93 %) and oxygen (65.99 %), while the microstructure image is shown in Figure 7.
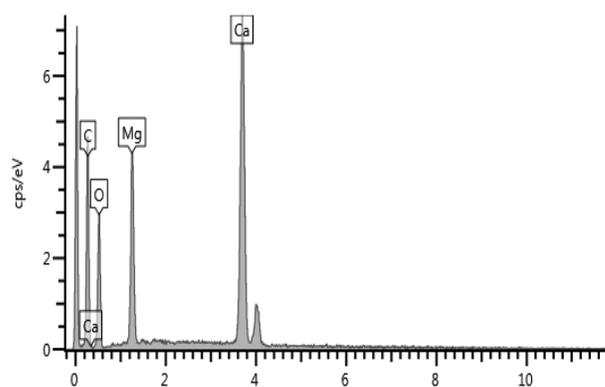

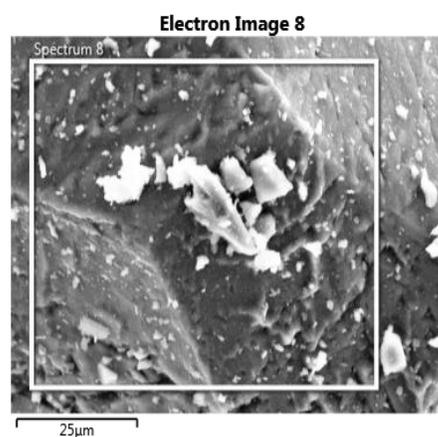**Figure 6.** *EDS Pattern of pink dolomite ore*   **Figure 7**. *EDS Image of pink dolomite ore*

Table 1. *Elemental composition of dolomite ore*

Element	O	Mg	Ca	Total
Atomic %	65.99	13.93	20.09	100

3.2 The effect of HNO₃ concentration on the reaction of dolomite

Dolomite reaction in HNO_3 solution is governed by the stoichiometric Equation 2:

$$CaCO_3.MgCO_{3(S)} + 4HNO_{3\ (aq)} \longrightarrow Ca(NO_3)_2 + Mg(NO_3)_2 + 2H_2O_{(l)} + 2CO_{2\ (g)} \qquad (2)$$

The equation of the reaction shows that two stages are involved, which are the reaction between Calcium carbonate and magnesium carbonate with HNO_3.

Figure 8 presents the plot of fractions of reacted dolomite with HNO_3 concentration between 0.5 and 2.5 M. It can be seen that the increase in acid concentration shows a positive effect on the fraction of reacted dolomite as reaction time increased. This is in agreement with the report by Baba et al. [1]. Pultar et al. [13] reported that increase in hydrogen ion (H^+) concentration leads to increase in the rate of dolomite dissolution. However, this present study has been able to establish a higher fraction of dolomite leaching of 0.995 at reduced leaching time of 60 min, HNO_3 concentration of 2.5 M and reaction temperature of 55 °C while Pultar et al. [13] recorded slightly above 0.8 fraction of reacted dolomite in 25 h, 40 °C and 0.1 M concentration. Baba et al. [1] reported fraction of reacted dolomite of 0.759 at 120 min in 2 M of HCl.
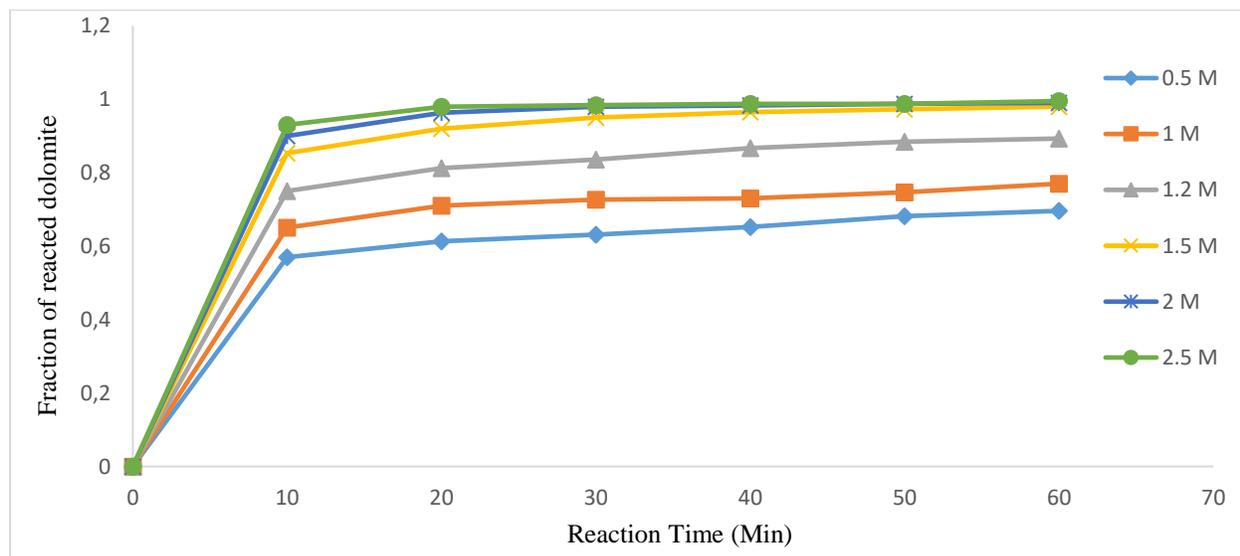

Figure 8. *Effect of HNO₃ concentration on the kinetic study of dolomite*
(3 g mass of dolomite, temperature of 55 °C)

Figure 9 shows that the fraction of reacted dolomite increased from 0.777 to 0.993 as the temperature increased from 30 to 70 °C. This could be attributed to the increase in the kinetic energy of the uncatalysted heterogeneous reaction system as more of the reactants were converted to products.
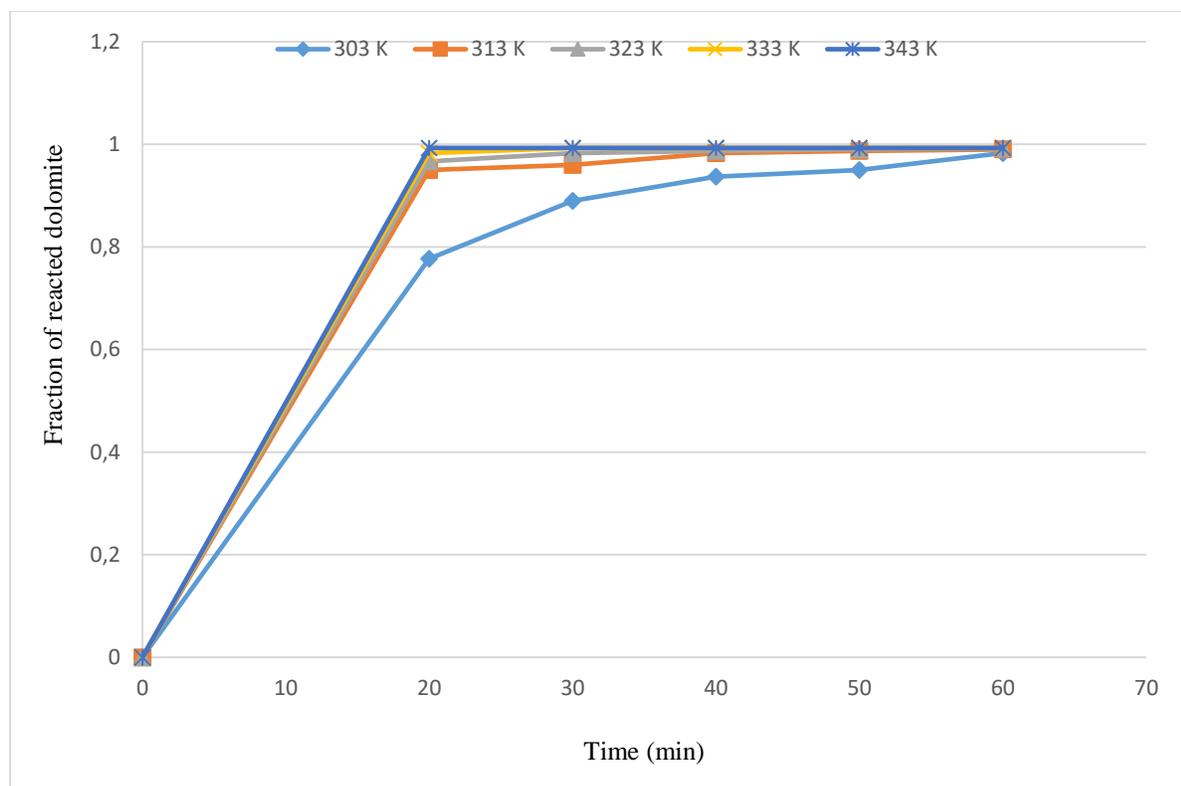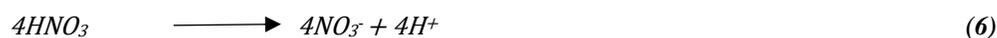
Figure 9. *Effect of temperature on the leaching efficiency of dolomite in (2.22 M HNO₃, 3 g mass of dolomite)*

3.3 Kinetic study

Based on bond breaking and formation between atoms in any chemical reaction, the reaction between dolomite and HNO₃ can be explained by the reaction mechanism developed in this study (Equations 3 to 9):

$$CaMg(CO_3)_2 \longrightarrow Ca(CO_3)_2 + Mg(CO_3)_2 \qquad (3)$$

$$Ca(CO_3)_2 \longrightarrow Ca^{2+} + CO_3^{2-} \qquad (4)$$

$$Mg(CO_3)_2 \longrightarrow Mg^{2+} + CO_3^{2+} \qquad (5)$$

$$4HNO_3 \longrightarrow 4NO_3^- + 4H^+ \qquad (6)$$

$$Ca^{2+} + 2NO_3^- \longrightarrow Ca(NO_3)_2 \qquad (7)$$

$$Mg^{2+} + 2NO_3^- \longrightarrow Mg(NO_3)_2 \qquad (8)$$

$$4H^+ + 2CO_3^{2+} \longrightarrow 2CO_2 + 2H_2O \qquad (9)$$

The reaction between dolomite and HNO₃ involves complex reactions. In order to have a more simplified model, a mathematical model using shrinking core model (SCM) was developed from the experimental data to explain the kinetics of the reactions. The heterogeneous reaction between dolomite and HNO₃ involves three steps:

1. Film diffusion control: this involves the migration of liquid film around solid particles [3]

$$X = 6bDC_A/P_oR_o^2t = k_1t \qquad (10)$$

2. Surface chemical reaction control:

$$1 - (1-x)^{1/3} = 6bDC_A/P_oR_o^2t = k_2t \qquad (11)$$

3. Ash product layer diffusion control:

$$1 + 2(1-x) - 3(1-x)^{2/3} = 6bDC_A/P_oR_o^2t = k_3t \qquad (12)$$

where ρ_o is the molar density of solid reactant (mol/m^3), Ro is the radius of a sphere (m), b is the stoichiometric coefficient of the solid, D is the effective diffusion coefficient (m^2/s) and C_A is the concentration of A in the bulk solution (mol/m^3), K_1, K_2, K_3 are rate constant for diffusion control, surface chemical reaction control and Product layer diffusion control, respectively. [2]

SCM was chosen based on the assumption that dolomite particles are spherical. The linearization of a plot of fractions of dolomite that reacted at various HNO_3 concentration and reaction temperature with the corresponding time were examined under the three SCM Equations (10), (11) and (12). The experimental data were tested for first line of best fits, which is also the slowest step as well as the rate determining step.

Table 2 presents the comparative values of apparent rate constants from the slops and the regression coefficient (R^2). The kinetics model equations show that the mechanism followed the order of ash product layer diffusion control > surface chemical reaction control > film diffusion controls. Therefore, the experimental data best fit the product layer diffusion control mechanism which is also the rate determining step. The natural logarithm of apparent rate reaction constants that were evaluated from the slope of Figure 10 were plotted against the natural logarithm of the acid concentrations.

Table 2. Correlation coefficient, R^2 and apparent rate constants at various temperature and concentration

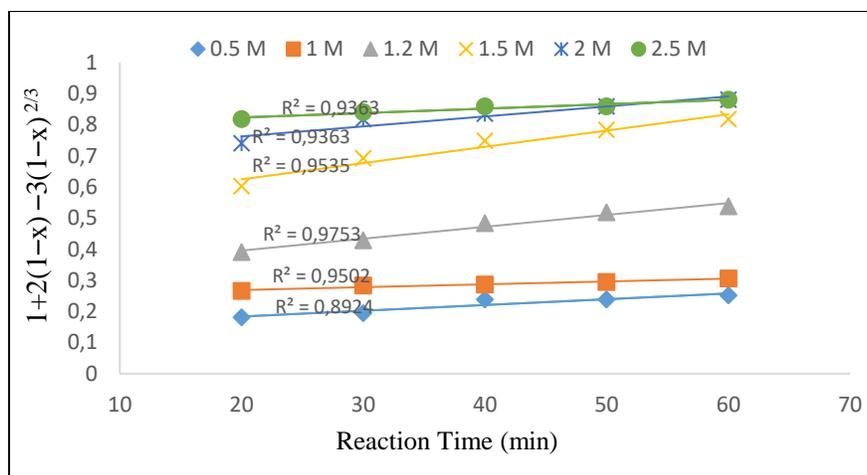| Process Variable	Kinetic Equation					
	X = k1t (Film Diffusion Control)		1 – (1–X)1/3 = k2t (Chemical Reaction Control)		1+2(1–X) – 3(1–X) 2/3 = k3t (Ash Layer Diffusion Control)	
Temp (°C)	$K_1 \times 10^{-3}$	R^2	$K_2 \times 10^{-3}$	R^2	$K_2 \times 10^{-3}$	R^2
30	4.72	0.867	8.078	0.9687	11.974	0.9804
40	1.07	0.8959	4.126	0.9313	5.05	0.9699
50	0.57	0.8147	2.833	0.9035	3.523	0.9397
60	0.2	0.5	1.318	0.5	1.608	0.7272
70	0	0	0	0	0	0
Conc (M)						
0.5	2.451	0.9782	1.415	0.9829	1.243	0.8924
1	2.04	0.8727	0.668	0.9482	1.42	0.9502
1.2	2.749	0.9198	2.559	0.9749	2.831	0.9753
1.5	2.311	0.8214	3.872	0.9154	3.505	0.9535
2	1.5	0.6721	2.719	0.9656	3.921	0.9363
2.5	0.997	0.6235	2.178	0.8327	3.942	0.9363

***Figure 10.** Plot of $1+2(1-x)-3(1-x)^{2/3}$ vs Reaction time at various HNO$_3$ concentration*

3.4 Order of reaction

The effect of acid concentration on the kinetics of reaction of dolomite in HNO$_3$ was examined by plotting (Figure 11) the natural logarithm of apparent reaction rate constants evaluated from the slope of Figure 10 against the natural logarithm of the concentrations. The order of reaction provides information on how fast or how slow a reaction will occur. Having established that the reaction mechanism was predicted by product layer diffusion control mechanism, Figure 11 was plotted using the model equation. Hence the slope was determined to be 0.9152, this shows that the reaction was first ordered with respect to hydrogen ion concentration. This is close to the 0.77 reaction order reported by Pultar et al. [13] while Baba et al. [1] reported a half reaction order for leaching of dolomite in HCl.
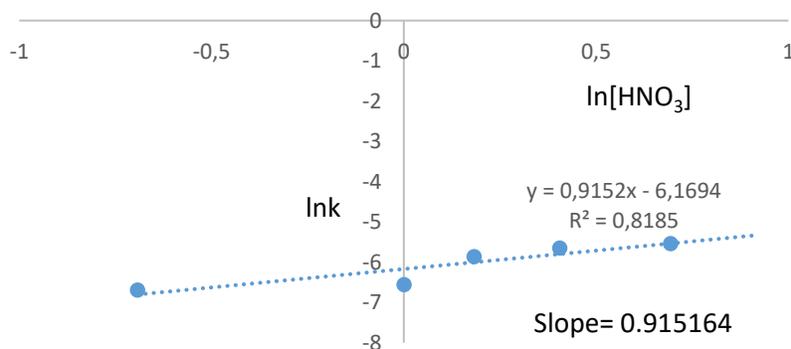

***Figure 11.** Plot of lnk Vs ln[HNO$_3$]*

3.5 Activation energy

The activation energy being the minimum energy required for a reaction to take place is given by the Arrhenius equation (Equation 12). The equation shows the relationship between temperature, activation energy (Ea) and the rate constant (K).

$$K = A \exp(-Ea/RT) \tag{13}$$

Where A is the frequency factor, R is the universal gas constant and T is the reaction temperature. In order to determine the activation energy required for the reaction between dolomite and HNO_3, the apparent rate constant evaluated from the slopes of Figure 10 were plotted against the inverse of the reaction temperature and this is shown in Figure 12. Using Equation (13) to get $\ln K = \ln A - Ea/RT$ (14). Comparing Equation (14) with Eqs. of straight-line $Y = mx + C$, therefore the slope of Figure 12 is equal to $-Ea/R$, that is $Ea = -$ slope x R.

$$Slop = -3200.1\ K,\ R = 8.3145\ Jmol^{-1}k^{-1}$$

$$Ea = -(-3200.1)\ K \times 8.3145\ J/mol\ k = 26605.6\ Jmol^{-1}k^{-1}$$

Activation energy of $26.605\ KJmol^{-1}k^{-1}$ was obtained for the reaction between dolomite and HNO_3. This value is below the activation energy range of 30 to $57\ KJmol^{-1}k^{-1}$ that was reported by Pultar et al. [13]. The lower activation energy shows an improvement on the reaction system as it is closely related to its rate. The lower the activation energy the higher the rate of the chemical reaction, this leads to increase in the fractions of dolomite that reacted. This is because molecules can only complete the reaction once they have reached the top of the activation energy barrier. The lower the barrier, the more molecules will have enough energy to make it over at any given moment [14]. This might be the reason for the high fractions of dolomite that reacted (0.995) within a short reaction time of 50 min as compared with the lower reaction fraction of 0.80 in 25 hours by Pultar et al. [13]. The activation energy ($26.605\ KJmol^{-1}$) in this study is slightly above the $20.77KJ/mol$ reported by Baba et al. [1] for the reaction between HCl and dolomite.

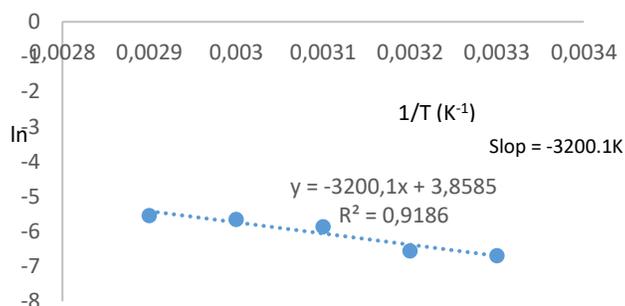***Figure 12.** Plot of lnk Vs 1/T (K^{-1})*

4 CONCLUSION

The EDS results show that Ikpeshi dolomite ore consists of calcium (20.09 %), magnesium (13.93 %) and oxygen (65.99 %). The reaction between dolomite and HNO_3 shows that the temperature and concentration have positive effect on the fractions of dolomite that reacted. Higher fraction of 0.995 dolomite reacted at reaction temperature of 55 °C, HNO_3 concentration of 2.5 M agitation speed of 200 rpm and leaching time of 60 min. The rate of the reaction was first ordered with respect to hydrogen ion concentration $[H^+]$ and the activation energy is $26.6\ KJmol^{-1}\ K^{-1}$. The rate of reaction of dolomite in HNO_3 follows a product layer diffusion control mechanism.

REFERENCES

[1] BABA, A.A., A.O. OMIPIDAN, F.A. ADEKOLA, O. JOB, A.G.F. ALABI, A. BARAL and R. SAMAL. Optimization study of a Nigerian dolomite ore dissolution by hydrochloric acid. *Journal of Chemical Technology and Metallurgy*. 2014, vol. 49(3), pp. 280–287. ISSN 1314-7471. Available from: https://dl.uctm.edu/journal/node/j2014-3/10-Baba-280-287.pdf

[2] AJEMBA, R.O. and O.D. ONUKWULI. Dissolution kinetics and mechanisms of reaction of Udi clay in nitric acid solution. *American Journal of Scientific and Industrial Research*. 2012, vol. 3(3), pp. 115–121. ISSN 2153-649X. DOI: 10.5251/ajsir.2012.3.3.115.121

[3] ONYEDIKA, G., C. NWOKO, A. OGUARAH and M. OGWUEGBU. Comparative kinetics of iron ore dissolution in aqueous HCl-HNO3 system. *Journal of Minerals and Materials Characterization and Engineering*. 2013, 1(4), pp. 153–159. ISSN 2327-4077. DOI: 10.4236/jmmce.2013.14026

[4] SADIK, C., O. MOUDDEN, A. EL BOUARI and I.-E. EL AMRANI. Review on the elaboration and characterization of ceramics refractories based on magnesite and dolomite. *Journal of Asian Ceramic Societies*. 2016, vol. 4(3), pp. 219–233. ISSN 2187-0764. DOI: 10.1016/j.jascer.2016.06.006

[5] ÑÚSTEZ-CASTAÑO, S.A., D.O. VILLAMIZAR-CASTRO and E.M. VARGAS-SOLANO. Evaluation of dolomite as catalyst in the transesterification reaction using palm oil (RBD). DYNA. 2019, vol. 86(209), pp. 180–187. ISSN 0012-7353. DOI: 10.15446/dyna.v86n209.74126

[6] ABALI, Y., S.U. BAYCA, K. ARISOY and A.I. VAIZOĞULLAR. Optimization of dolomite ore leaching in hydrochloric acid solutions. *Physicochemical Problems of Mineral Processing*. 2011, vol. 46, pp. 253–262. ISSN 0137-1282. Available from: http://www.journalssystem.com/ppmp/pdf-79072-15098?filename=Optimization%20of%20dolomite.pdf

[7] TRIPATHY, S.K., Y. RAMA MURTHY, L. PANDA, V. SINGH, P.K. BANERJEE and A. BHATNAGAR. A review on dolomite: Genesis, application and processing. *Journal of Mines, Metals and Fuels*. 2013, vol. 61(4), pp. 93–102. ISSN 0022-2755. Available from: https://www.academia.edu/21197326/A_review_on_dolomite_Genesis_application_and_processing

[8] SIVRIKAYA, O. A study on the physicochemical and thermal characterization of dolomite and limestone samples for use in iron making and steelmaking. *Ironmaking and Steelmaking*. 2018, vol. 45(8), pp. 764–772. ISSN 0301-9233. DOI: 10.1080/03019233.2017.1337264

[9] DING, Y., G. ZHANG, H. WU, B. HAI, L. WANG and Y. Qian. Nanoscale magnesium hydroxide and magnesium oxide powders: control over size, shape and structure via hydrothermal synthesis. *Chemistry of Materials*. 2001, vol. 13(2), pp. 435–440. ISSN 0897-4756. DOI: 10.1021/cm000607e

[10] DUHAIME, P., P. MERCILLE and M. PINEAU. Electrolytic process technologies for the production of primary magnesium. *Transactions of the Institutions of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy*. 2002, vol. 111(May/August), pp. 53–55. ISSN 0371-9553. DOI: 10.1179/mpm.2002.111.2.53

[11] MUBAROK, M.Z. and C.A. KURNIAWAN. Synthesis of magnesia powder from East Java dolomite through leaching, precipitation and calcination. *Advanced Materials Research*. 2015, vol. 1112, pp. 550–554. ISSN 1662-8985. DOI: 10.4028/www.scientific.net/AMR.1112.550

[12] SOLIHIN, I. and M.Z. MUBAROK. Dissolution profile of dolomite in chloric acid solution: The effect of chloric acid concentration and pulp density. In: *AIP Conference Proceedings, vol 1964: 1st International Seminar on Metallurgy and Materials: Metallurgy and Advanced Material Technology for Sustainable Development, ISMM 2017: October 24–25, 2017, Jakarta, Indonesia*. 2018. ISBN 978-073541669-7. DOI: 10.1063/1.5038304

[13] PULTAR, M., J. VÍDENSKÝ and I. SEDLÁŘOVÁ. Study of the reaction between dolomite and nitric acid. *Physicochemical Problems of Mineral Processing*. 2019, vol. 55(2), pp. 370–379. ISSN 1643-1049. DOI: 10.5277/ppmp18140

[14] KHAN ACADEMY. Activation energy, transition state, and reaction rate. *Khan Academy* [online]. 2018 [cit. 2020-01-02]. Available from: https://www.khanacademy.org/science/high-school-biology/hs-energy-and-transport/hs-enzymes/a/activation-energy