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Study of the reaction between dolomite and nitric acid

Martin Pultar, Jan Vidensky, Ivona Sedlarova

Department of Inorganic Technology, University of Chemistry and Technology, Technicka 5, 166 28 Prague 6

Corresponding author: martin.pultar@vscht.cz (Martin Pultar)

Abstract: This paper is focused on the kinetics of the reaction between natural dolomite and diluted solutions of nitric acid at various temperatures. All experiments were carried out in a semi-batch reactor with an approximately constant nitric acid concentration using the pH-stat titration method. The reaction was studied in the temperature range from 293 to 353 K and the nitric acid concentration in the range from 0.001 to 0.200 mol dm⁻³. The strong effects of both temperature and nitric acid concentration were observed. The determined fractional values of the apparent reaction order (0.39 to 0.75) indicate a very complex reaction mechanism. In the studied concentration range, the values of the apparent activation energy increase from 30 to 58 kJ mol⁻¹. Based on these data it can be assumed that the reaction takes place in the transitional regime with the stronger influence of chemical reaction. This assumption was verified by calculation of the nitric acid concentration on the surface of the dolomite grain using Sherwood criterion equation. The change in the role of the rate-controlling step was found for highly diluted solutions (< 0.010 mol dm⁻³ HNO₃).

Keywords: dolomite, nitric acid, kinetics, dissolution, shrinking core model

Introduction

Dissolution of dolomite as a carbonate raw material in aqueous solutions of various pH can be considered as an interdisciplinary topic. Published geological studies are focused on the processes occurring at the contact of underground and surface water of different composition with the sedimentary carbonate rock layers. These processes can be generally described as very complex reactions between all compounds located at the interface of the solid and liquid phases. Many authors studying this subject refer to the fundamental publication written by Busenberg and Plummer (1982). A wide group of researchers tried to set and simulate temperature and pressure conditions which occur in different depths of the Earth's crust. Specific information and results can be found in many publications (Herman and White (1985), Chou et al. (1989), Orton and Unwin (1993), Pokrovsky et al. (2005), Zhang et al. (2007)).

The processes for oil and gas extraction represent another field where the knowledge of the kinetics of carbonates (including dolomite) and mineral acids (mostly hydrochloric acid) reactions may be useful. The effect of this process is a partial destruction of the carbonates layers in the oil and gas deposits. The most comprehensive published papers were written by Lund et al. (1973). The analogous direction of interest was followed by other authors (Gautelier et al. (1999), Taylor et al. (2004)).

Another significant field where the studied kinetics plays an important role is inorganic industry. In most cases, reactions of carbonates (as raw or secondary raw material) with mineral acids represent an initial technological step in the whole process. In these technologies, dolomite is (especially for the inland states without suitable magnesite deposits) the strategic magnesium source for the still expanding production of magnesium fertilizers and other magnesium compounds. Based on the literature search, it follows that despite a large number of papers dealing with the dolomite (or other raw materials containing magnesium) – hydrochloric acid reaction system (Raschman and Fedorockova (2006, 2008), Fedorockova and Raschman (2008), Yildirim (2008), Yildirim and Akarsu (2010), Altiner et

al. (2016), etc.), there is a significant lack of published studies dealing with the dolomite (or magnesite) – nitric acid system. The last mentioned issue was studied by Vyborny and Madron (1989), Abdel-Aal (1995), Abdel-Aal and Rashad (1997), Köse (2012).

Reactions of dolomite with mineral acids also occur during the dolomitic phosphate and bauxite ore enrichment process (Perri and Tubiello (1963), Laird and Hanson (1994), Guan et al. (2017)). These processes are based on the significant difference in the dissolution rates of dolomite and the second mineral. Nowadays, fine-milled dolomite is also often used in the agriculture industries for the soil acidity decrease, and its large amounts are consumed in the ammonium nitrate production plants. During this production process, fine-milled dolomite is added into a melt of this salt and reacts in a quite large extent with nitric acid generated during the ammonium nitrate decomposition (Jäger and Hegner (1987), Rubtsov et al. (2005)). This reaction plays a key role in the explosiveness reduction of that system.

This paper is dealing with the dolomite dissolution in nitric acid. The reaction under study plays important role in the industrial fertilizers production. In this field, nitrate technologies are significant mainly due to the fact that very little or no waste is generated. Dolomite is one of important raw material that is possible to treat using nitrate technology and make magnesium available as an important biogenic element. Its presence is essential in nutrition of people, animals and plants. In the Czech Republic, and also in number of other countries, there is a significant lack of available magnesium in soils while its content further decreases due to the soil acidification. Nitrates are suitable compounds for magnesium supplements to soil unlike chlorides and sulphates. Magnesium – calcium fertilizer with its specific effects, produced by dissolution of dolomite using nitric acid, can be therefore seem as a great benefit from economic and ecological points of view. The goal of the paper is to assess kinetic parameters of the reaction under the specific conditions where the partially reacted dolomite grains are surrounded by diluted nitric acid (< 1.5 wt. %) in a large excess. Knowledge of the reaction kinetics under these limiting conditions is crucial for all mentioned industrial applications and plays a key role in the design of the industrial decomposition reactors.

Experimental

Materials

The kinetics was studied using natural dolomite from Vrchlabi (Czech Republic). After dry milling of particulate dolomite using industrial hammer and disc mills and dry screening, the fraction – 0.40 + 0.50 mm in diameter was prepared. Basic physicochemical characteristics of the selected fraction are given in Table 1. From XRD analysis (Fig. 1) it is obvious that the raw material contains especially dolomite $\text{CaMg}(\text{CO}_3)_2$. The content of nitric acid-insoluble admixtures in dolomite was determined by a long-time dissolution as approximately 2.5 wt. %. It was found that the used dolomite is an almost non-porous material with a low value of the specific surface area. In all experiments, analytical reagent grade of nitric acid (Penta) and distilled water were used.

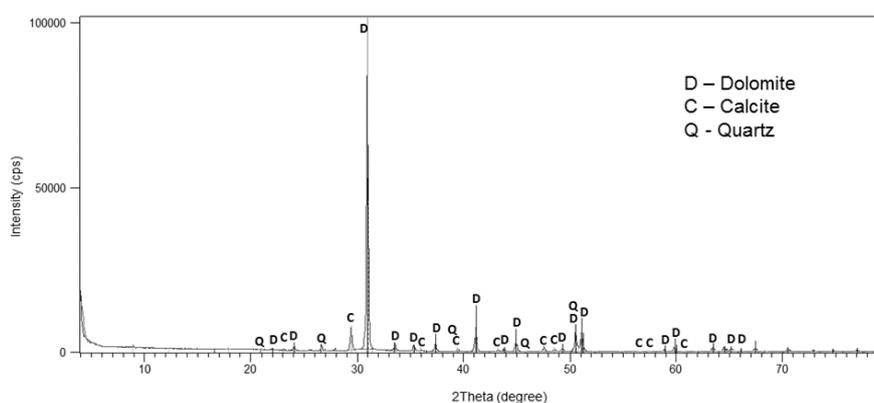
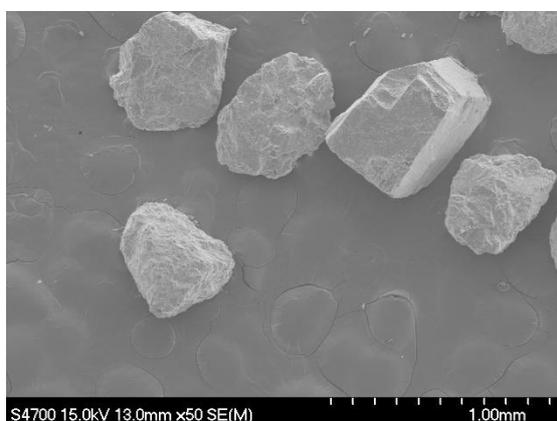
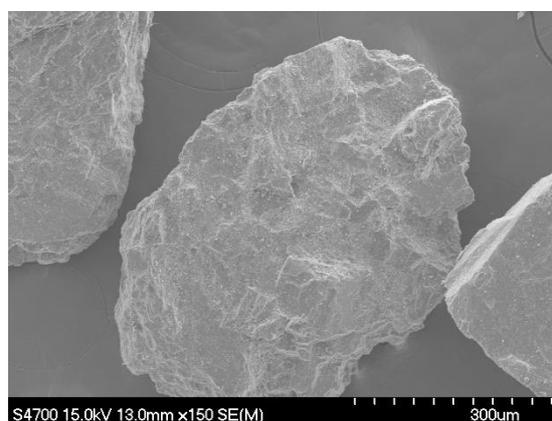


Fig. 1: XRD pattern of natural dolomite from Vrchlabi, Czech Republic

Table 1. Basic characteristics of natural dolomite from Vrchlabi

DOLOMITE VRCHLABI		Instrumentation
Particle size (mm)	- 0.40 + 0.50	AS 200 (Retsch)
Spec. surface area (m ² g ⁻¹)	0.16	3Flex Surface Characterization (Micromeritics)
Porosity (%)	5.7	AutoPore IV 9500 (Micromeritics)
Skeletal density (kg m ⁻³)	2 681	Pycnomatic ATC-Multi (Porotec)
XRD Phase composition (wt. %)		
CaMg(CO ₃) ₂	95	PANalytical X'Pert PRO
CaCO ₃	4	
SiO ₂	1	

**Fig. 2.** SEM picture of dolomite particles (- 0.40 + 0.50 mm).**Fig. 3.** SEM picture of dolomite particles (- 0.40 + 0.50 mm) - detailed picture of single particle.

Experimental procedure

The kinetics of dolomite dissolution in nitric acid was studied in the temperature range from 293 to 353 K with nitric acid concentration from 0.001 to 0.200 mol dm⁻³ at 200 – 800 rpm. All kinetic experiments were carried out in an open isothermal semi-batch reactor represented by an 800 cm³ glass flask (86 mm in diameter) placed in a bath thermostat (Julabo 12). The reactor was filled by 600 cm³ fresh solution of nitric acid before each experiment. The reaction mixture was stirred using a 4-blade agitator (40 mm in diameter). After reaching the required temperature, a small amount (0.5 g) of natural dolomite was added. The reaction course was observed by the pH-stat titration method (a titration unit TitroLine Alpha TA 50 plus (Schott); a combined glass pH-electrode (HC 104, Theta '90)). The automatic titration unit dosed small volume of the more concentrated nitric acid solution to keep the pH value on the initial level while pH of the solution increased due to the outgoing reaction. The added volume and the titration speed depended on the dolomite dissolution rate.

The dependence of the batched volume of nitric acid on time was then used for the calculation of the conversion degree of dolomite (η_D) in time. From gained dependencies, the quantity $(d\eta_D/d\tau)_{\eta \rightarrow 0}$ for the beginning of the reaction was evaluated. A linear part of each reaction isotherm was fitted by a straight line. The slope of this line was estimated using the linear regression and the least square method. The slope was equal to the hidden value of $(d\eta_D/d\tau)_{\eta \rightarrow 0}$ that was used in the next data processing.

Results and discussion

Effect of stirring speed

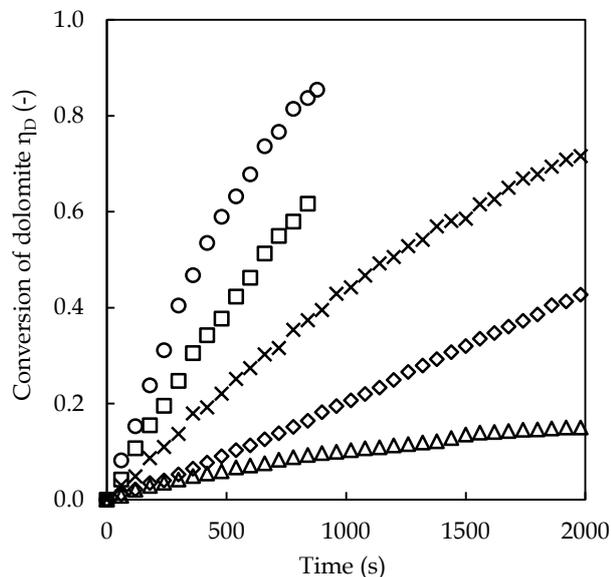
At the beginning of this study, a series of measurements studying the effect of stirring speed on the reaction course was provided. It was necessary to eliminate the effect of the external mass transfer. For this purpose, the dolomite – nitric acid reaction was studied at constant reaction conditions and the various rotation speed of the stirrer: 200, 400, 600 and 800 rpm. The strong increase in values of the dolomite conversion degree at given time was observed in the range of low stirring speed (from 200 to 400 rpm) only. The subsequent increase of the stirring speed in the range from 400 to 800 rpm did not significantly affected the $(d\eta_D/dt)_{\eta \rightarrow 0}$ values.

Based on these results it was decided to use the stirring speed 600 rpm for the subsequent experiments. This value ensured the maintenance of the desired hydrodynamic conditions when the dolomite grains are fluidized and surrounded by nitric acid for the whole reaction time. Similar behaviour was published in many papers dealing with the dolomite dissolution in mineral acids (Vyborny and Madron (1989), Özbek et al. (1999), Yildirim (2008)).

Effect of temperature and nitric acid concentration

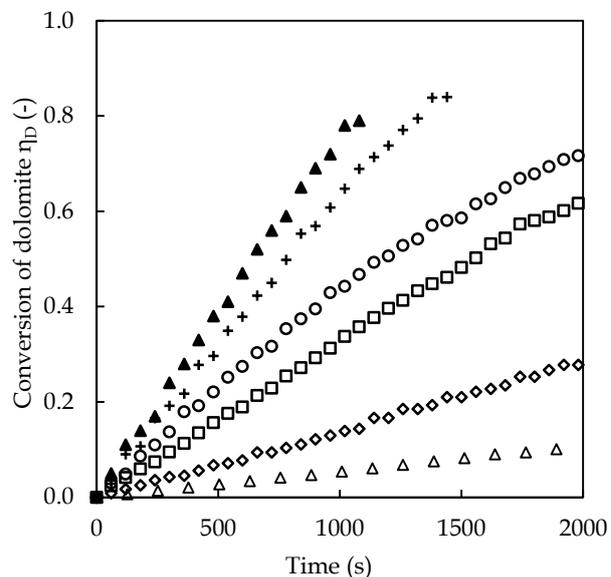
Effect of temperature on the reaction course was studied in the range from 293 K to 353 K. The studied reaction is very sensitive to temperature, the values of the $(d\eta_D/dt)_{\eta \rightarrow 0}$ increased with rising temperature (one of measured dependencies is shown in Fig. 4). This trend is common for this type of irreversible heterogeneous non-catalysed reaction (Lund et al. (1973), Vyborny and Madron (1989), Abdel-Aal (1995), Fedorockova and Raschman (2008)).

Effect of nitric acid concentration was the next monitored parameter. In the whole concentration range from 0.001 to 0.200 mol dm⁻³, a positive influence of increasing concentration on the values of $(d\eta_D/dt)_{\eta \rightarrow 0}$ was observed, as it is shown in Fig. 5.



○ 333 K □ 323 K × 313 K ◇ 303 K ▲ 293 K

Fig. 4. Effect of temperature on the conversion degree of dolomite vs. time ($c_A = 0.050 \text{ mol dm}^{-3}$)



▲ 0.200 mol dm⁻³ + 0.100 mol dm⁻³ ○ 0.050 mol dm⁻³
 □ 0.025 mol dm⁻³ ◇ 0.005 mol dm⁻³ △ 0.001 mol dm⁻³

Fig. 5. Effect of nitric acid concentration on the conversion degree of dolomite vs. time ($T = 313 \text{ K}$)

Kinetic study of the reaction system

The studied reaction between dolomite and nitric acid (Eq. (1)) is an exothermic reaction ($\Delta H_r = -61 \text{ kJ mol}^{-1}$) and belongs to the group of the irreversible heterogeneous non-catalysed reactions.



This reaction represents a very complex system which includes partial processes located at the solid – liquid interface like transport of reagents and products through phase interphases, adsorption and desorption on the surface of the solid phase, chemical reactions and also heat transport. The detailed description of the mechanism of this reaction can be quite complex. Therefore, the mathematical description often uses simplified models, which allow evaluating the kinetics directly from the experimental data.

Due to low porosity of used raw dolomite and high solubility of all products, the shrinking core model for the non-porous spherical grain was used for the description of the studied reaction. For the non-porous grain, the chemical reaction is located on the outer surface of the solid phase. The main presumptions of the applicability of the shrinking core model (SCM) are described in detail in many publications (Levenspiel (1962), Vidensky and Glaser (1987), Vyborny and Madron (1989), Raschman and Fedorockova (2006), Yildirim (2008)). All quantities used in the presented model SCM have physical meaning.

From the macrokinetic point of view, the overall evaluation of the system in this case depends on two rate-controlling processes – chemical reaction and/or external mass transfer. The rate of consumption of nitric acid on the surface of the dolomite grain r_{AS} may be defined by Eq. (2)

$$r_{AS} = - \frac{1}{S} \cdot \frac{dN_A}{d\tau} = k_S \cdot c_{AS}^n \quad (2)$$

where S is the outer reaction surface, N_A is the amount of nitric acid, τ is time, k_S is the reaction-rate constant per unit of dolomite surface area, c_{AS} is the concentration of nitric acid on the dolomite surface and n is the apparent reaction order. The external mass transfer rate j_{AS} is defined as Eq. (3)

$$j_{AS} = k_{mA} \cdot (c_A - c_{AS}) \quad (3)$$

where k_{mA} is the mass transfer coefficient for nitric acid and c_A is the bulk concentration of nitric acid.

In the case of the studied reaction, it was supposed that the chemical reaction is a rate-controlling step. This situation occurs as soon as the value of the reaction-rate constant k_S is significantly lower than the value of the mass transfer coefficient k_{mA} , thus $k_S/k_{mA} \approx 0$. Nitric acid concentration on the dolomite surface is therefore the same as in the bulk. The overall reaction rate can be then defined as Eq. (4). This relation is evaluated based on the Eq. (2) and the balance equation for the studied system.

$$r_{AS} = - \frac{1}{S} \cdot \frac{dN_A}{d\tau} = \frac{1}{S} \cdot \frac{a \cdot m_{D0}}{b \cdot M_D} \cdot \frac{d\eta_D}{d\tau} = k_S \cdot c_A^n \quad (4)$$

where a , b are the stoichiometric coefficients of nitric acid and dolomite, respectively (in Eq. (1)); m_{D0} is an initial amount of dolomite, M_D is the molar mass of dolomite and η_D is the conversion degree of dolomite.

The measured dependencies were characterized using the appropriate kinetic parameters (the apparent activation energy and the apparent reaction order). Their values were calculated using linearization of the Eq. (4) with respect to the beginning of the reaction (the subscript “ $\eta \rightarrow 0$ ”) and related to the initial specific surface of the dolomite grains S_{D0} .

The concentration dependence was characterized by the apparent reaction order n_Z calculated from the experimental data obtained as:

$$\ln \left(\frac{d\eta}{d\tau} \right)_{\eta \rightarrow 0} = \ln \left(\frac{b \cdot S_{D0} \cdot M_D \cdot k_S}{a} \right) + n_Z \cdot \ln(c_A) \quad (5)$$

The process of the n_Z evaluation is illustrated in the Fig. 6. The obtained values of n_Z (see Table 2) are in the range from 0.39 at 293 K to 0.75 at 353 K. The values of n_Z for 343 and 353 K are burdened by a greater error caused by the high reaction rate. Due to the limitations of the pH-stat technique, higher concentrations of nitric acid cannot be measured at these temperatures ($\text{pH} \leq 0$). Therefore, to obtain enough points for the n_Z evaluation, more concentrations in the range 0.001 and 0.010 mol dm⁻³ were measured (0.002, 0.003 and 0.007 mol dm⁻³). After consideration of a non-ideal behavior of the nitric acid solutions, it was useful to convert concentration to activity a_A . The values of activity coefficients were found in the literature (Landolt and Börnstein (1969), Perry and Green (1998)). The values of n_Z obtained using the values of activity a_A are somewhat higher as it can be observed from Table 2. Based on these values, it may be assumed that the reaction proceeds via more complex reaction mechanism.

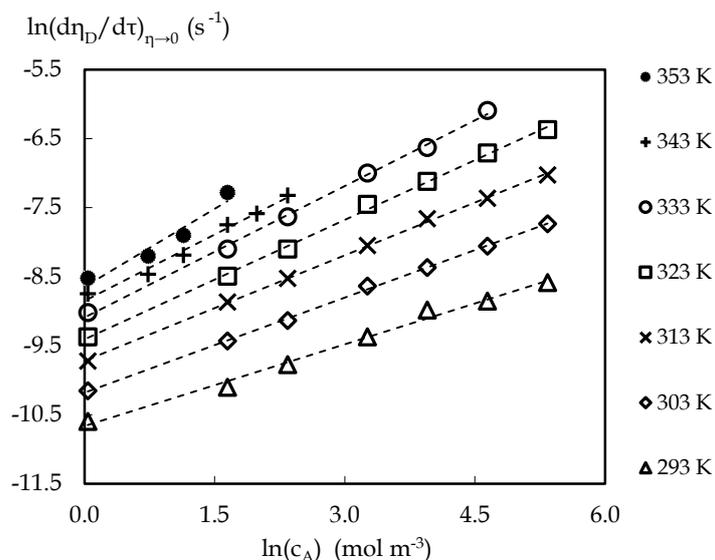


Fig. 6. Evaluation of the values of apparent reaction order for the studied reaction temperatures

Table 2. Values of n_Z obtained from concentration (c_A) and activity (a_A) of nitric acid solutions

Temperature (K)	293	303	313	323	333	343	353
Apparent reaction order $n_Z(c_A)$	0.39	0.46	0.50	0.58	0.64	0.64	0.75
Apparent reaction order $n_Z(a_A)$	0.45	0.51	0.57	0.65	0.69	0.66	0.77

As it was mentioned before, there is a lack of studies dealing with the dolomite – nitric acid reaction system. However, the fractional values of the reaction order were published for the dolomite dissolution in other acids, especially in hydrochloric acid solutions (Lund et al. (1973), Busenberg and Plummer (1982), Chou et al. (1989), Gautelier et al. (1999), Taylor et al. (2004), Yildirim (2008), Yildirim and Akarsu (2010)). These researchers also found the increasing tendency of the reaction order values with increasing temperature. On the contrary, Vyborny and Madron (1989) determined the first order reaction of the dolomite dissolution in nitric acid. Nevertheless, they have worked with more concentrated nitric acid solutions.

The apparent activation energy E_Z that was used for evaluation of the temperature dependence was calculated from the following equation.

$$\ln\left(\frac{dn}{dt}\right)_{\eta \rightarrow 0} = \ln\left(\frac{b \cdot S_{D0} \cdot F \cdot M_D \cdot c_A^n}{a}\right) - \frac{E_Z}{RT} \quad (6)$$

where F is the pre-exponential coefficient, R is the general gas constant and T is the absolute temperature. The used relation was evaluated based on the Eq. (4) and the Arrhenius expression for the temperature dependence of k_s . It was supposed that the bulk nitric acid concentration (c_A) was constant.

From the experimental data, the values of the apparent activation energy E_Z were evaluated (see Fig. 7 and Table 3). The determined values increase from 30.1 kJ mol⁻¹ to 57.9 kJ mol⁻¹ under the studied reaction conditions. From these values of E_Z it may be assumed that the overall process is primarily controlled by the chemical reaction, however, it is not possible, especially for the lower acid concentration, to eliminate the influence of the external mass transport.

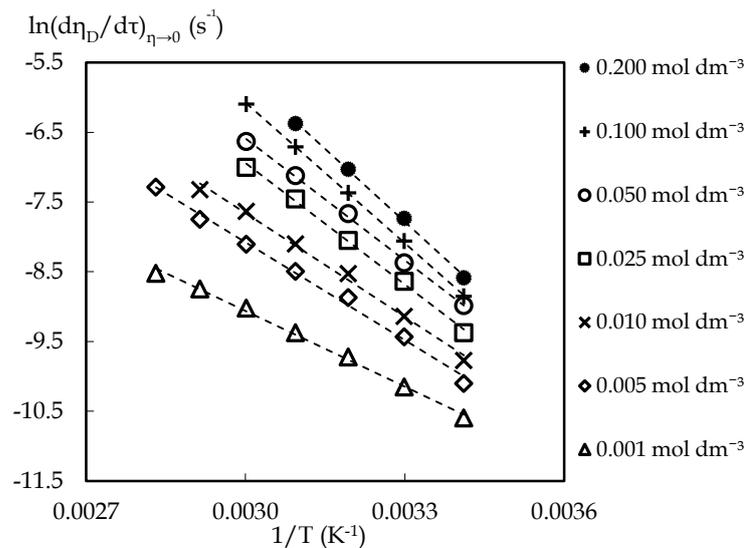


Fig. 7. Evaluation of the values of apparent activation energy for the studied concentrations of nitric acid

Table 3. Values of the apparent activation energy obtained under the studied concentrations of nitric acid

c_A (mol dm ⁻³)	0.001	0.005	0.010	0.025	0.050	0.100	0.200
E_z (kJ mol ⁻¹)	30.1	38.9	43.3	48.3	48.5	55.8	57.9

There is a quite good agreement with the previously published result by Vyborny and Madron (1989). They found the value of 44 kJ mol⁻¹ for the dolomite dissolution in nitric acid. Similar values were published by Gautelier et al. (1999) (from 15 to 46 kJ mol⁻¹) and Yildirim (2008) (32 kJ mol⁻¹) for the dolomite – hydrochloric acid system. Lund et al. (1973) and Busenberg and Plummer (1982) found higher values of the apparent reaction energy in the range 30 – 90 kJ mol⁻¹ and 61.5 kJ mol⁻¹, respectively, for the same reaction system. All mentioned authors also evaluated the chemical reaction as the main rate-controlling step.

For the verification of the previous statement that the chemical reaction has a major influence on the dissolution process as a rate controlling step, the model values of the nitric acid concentration on the dolomite surface c_{AS} were calculated. At first, the mass transfer coefficient k_{mA} was estimated using Sherwood number Sh which is defined by the Eq. (7)

$$Sh = \frac{k_{mA} \cdot d}{D_{Am}} \quad (7)$$

where d is the diameter of the dolomite grain and D_{Am} is the mean diffusion coefficient of nitric acid under given conditions. The Sherwood number was estimated using the appropriate criterion equation that depends on the reaction system properties and applied experimental arrangement. For the studied case, the forced convection around spherical particle, the equation suggested by Cussler (1984) (Eq. (8)) was used.

$$Sh = 2 + 0.6 \cdot \left(\frac{d \cdot v}{\nu_A} \right)^{1/2} \cdot \left(\frac{\nu_A}{D_{Am}} \right)^{1/3} \quad (8)$$

where v is the mean velocity of particle motion (dolomite grains) and ν_A is the kinematic viscosity of the nitric acid solution (Landolt and Börnstein (1969), Cussler (1984), Perry and Green (1998)).

Determined values of the mass transfer coefficients were then used for the calculation of c_{AS} (Eq. (3)) and consequently of the ratio c_{AS}/c_A . The calculations were provided for nitric acid concentrations 0.001, 0.010, 0.100 and 0.200 mol dm⁻³ and reaction temperatures 293, 313 and 333 K (see Fig. 8).

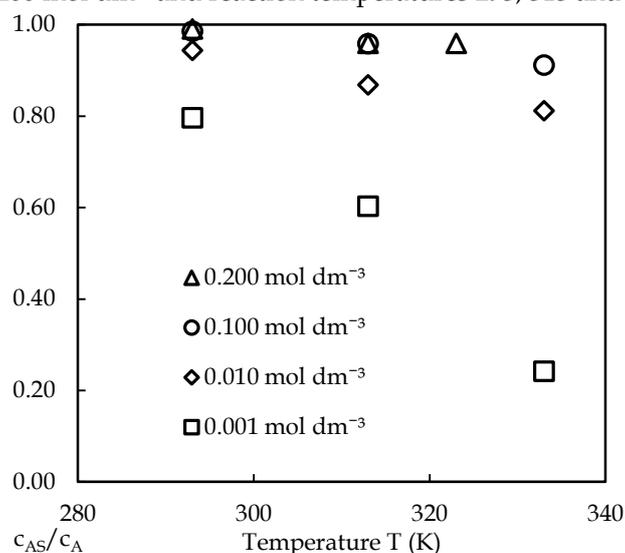


Fig. 8. Effect of temperature and nitric acid concentration on the c_{AS}/c_A ratio

If the ratio c_{AS}/c_A approaches to 1 it indicates that $c_{AS} \approx c_A$. This denotes the transport of the reagent from the bulk phase to the surface of the dolomite grains does not represent a significant barrier and the chemical reaction is the rate-controlling step. On the other hand, when c_{AS}/c_A approaches to 0, then the external mass transport is rate-controlling. For higher concentrations (0.010 mol dm⁻³ and higher), the c_{AS}/c_A values are in the close range 0.81 – 0.99 at the whole temperature range. Therefore, the chemical reaction on the surface of the dolomite grain is in this case the main rate-controlling step. However, at very low concentrations (lower than 0.010 mol dm⁻³), the c_{AS}/c_A ratio rapidly decreases with increasing temperature to the low value of 0.24 at 333 K. At these reaction conditions (high reaction temperature and a highly diluted nitric acid solution), it can be therefore assumed the influence of the external mass transport may play a significant role. This behaviour may be also indicated by an obvious decrease of the apparent activation energy value. Only Gautelier et al. (1999) reported similar result, but in the dolomite-hydrochloric acid system and their c_{AS}/c_A values were somewhat higher (≈ 0.60) compared to our results.

Conclusions

In this paper, the reaction between raw dolomite and diluted nitric acid was studied. The reaction conditions were chosen with respect to the simulation of the state which can be characterized by the presence of the partially reacted dolomite grains with excess of highly diluted nitric acid, hence the study is dealing with the dolomite post-reaction.

The reaction was studied in the temperature range from 293 to 353 K with nitric acid concentration from 0.001 to 0.200 mol dm⁻³ under controlled hydrodynamic conditions. The shrinking core model (SCM) was applied. It was found the nitric acid concentration has a positive effect on the reaction course. The values of the apparent reaction order evaluated from the experimental data are estimated in the range from 0.39 (293 K) to 0.75 (353 K). From these values it could be assumed the reaction proceeds via more complex reaction mechanism. The strong effect of temperature on the dolomite conversion degree in the whole studied range is also observed. The calculated values of the apparent activation energy increase from 30.1 kJ mol⁻¹ (0.001 mol dm⁻³) to 57.9 kJ mol⁻¹ (0.200 mol dm⁻³). From the macro kinetic point of view, it may be therefore assumed the dissolution process is controlled primarily by the chemical reaction with a small contribution of the external mass transport. However, c_{AS}/c_A values indicate stronger influence of the external mass transport on the reaction rate for the lower nitric acid concentrations (< 0.010 mol dm⁻³) and high temperatures. Under these conditions, the external mass transport may be the rate-controlling step.

The change in the role of rate-controlling step will influence the reaction rate of the dolomite dissolution under the mentioned limiting conditions. Therefore, this fact may play a key role in the design and optimization of the whole process.

Acknowledgements

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