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Effects of pH and acid anions on the dissolution kinetics of MgO

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ABSTRACT

The kinetics of the dissolution of particulate sintered polycrystalline MgO under *advanced* kinetic regime conditions were investigated, with special regard to the effects of concentration of H^+ ions, temperature and the type of the inorganic acid used (HCl, HNO_3 and H_2SO_4). It was observed that the rate of chemical dissolution of MgO accelerated with increase in both concentration of H^+ ions (from 10^{-4} to 10^{-2} M) and temperature (from 25 to 60 °C). The overall process of MgO dissolution was found to be controlled by the surface chemical reaction of MgO with H^+ ions. The presented values of the reaction order for H^+ ions are consistent, allowing for experimental error, with current kinetic theories and most other experiments. However, the rate-controlling step could not be assigned unambiguously, because the same value of the reaction order for H^+ ions can be predicted by various theories for different rate-determining steps. Measured values of the reaction order for H^+ ions are indicative that the rate is limited by the second protonation reaction, i.e. the slow reaction of surface hydroxide with a second proton. Though the reaction order for H^+ ions seems not to be affected by the type of acid used, the apparent activation energy changes in the order $HCl \leq HNO_3 < H_2SO_4$. Higher values of activation energy obtained for H_2SO_4 could indicate that surface chemical reaction is controlled by different reactions between surface anions and protons created by dissociation of H_2SO_4 and HCl (or HNO_3).

1. Introduction

Dissolution of oxides by the action of acidic aqueous solutions plays an important role in a wide variety of processes, including for example environmental and geochemical processes, hydrometallurgy, corrosion, catalysis and drug design.

When an oxide is dissolved, the O^{2-} incipiently coordinated to cations in an oxide layer will be replaced by H_2O, OH^- or other ligands when the cations are transferred into solution. The key to identifying the overall rate of reaction lies in understanding the factors that affect the elementary steps. The following steps are well-known: (a) mass transport of solutes (H^+, OH^-, ligands) to the oxide surface; (b) surface attachment of the solutes (adsorption or surface complex formation); (c) various surface chemical reactions (inter-lattice transfers, etc.); (d) detachment of products from the surface; and (e) mass transport of dissolved products into the bulk of the solution [1].

Despite the fact that several reviews on this topic have been published during the last three decades [2–6], the general principles governing the kinetics of the dissolution of oxides are not sufficiently known. A major difficulty in attempting to derive a general concept of the mechanism of oxide leaching is that single oxides have seldom been intensively studied, and the range of conditions for the individual oxides varies from one author to the next [2].

Magnesium oxide is a model oxide, ideal for case studies, because it combines relative ease of theoretical and experimental studies with widespread applicability to both natural [4,6–8] and industrial systems [9–14]. The "case study" character of MgO relates to the fact that: (a) in the case of a predominantly ionic oxide such as MgO the charge characteristics are not rate-determining [5,15]; (b) periclase (MgO) forms rock salt-like crystals and has a relatively simple electronic structure that can be modelled using *ab initio* calculations [8,16,17]; (c) MgO prepared by burning magnesium in air produces small cubic crystals with a very high degree of perfection [15,18–20]; (d) MgO is one of the few oxides that allows investigation of dissolution rates and mechanisms at room temperature.

Chemical dissolution of periclase (MgO) has been intensively studied. Generally, a very good correlation between experiment and theory is observed. The overall rate can be controlled by diffusion of dissolved reactants/products or by the surface reaction, dependent on the reaction conditions [5,6,18,20–24]. Notwithstanding the extensive literature on the measurement and interpretation of the kinetics of magnesium oxide dissolution in various acidic aqueous solutions [5,6,15,16,18,20–26], the rate-controlling step cannot be assigned unambiguously. Many authors have shown that the empirical rate law $r = k[H^+]^n$ for MgO dissolution exhibits a fractional rate

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Nomenclature

a_{H^+w}	activity of H^+ ions on the particle surface
E	apparent activation energy ($J\,mol^{-1}$)
$[H^+]^0$	initial concentration of H^+ ions ($mol\,dm^{-3}$)
k_{LS}	mass transfer coefficient ($m\,s^{-1}$)
k_S	apparent reaction-rate constant ($mol\,m^{-2}\,s^{-1}$)
k_0	frequency factor ($mol\,m^{-2}\,s^{-1}$)
m^0_{MgO}	initial amount of MgO (g)
M_{MgO}	mole mass of MgO = 40.3 ($g\,mol^{-1}$)
n	apparent order of the overall surface chemical reaction (1)
N	number of leaching runs
pH^0	initial value of pH corresponding to $[H^+]^0$
r'	dissolution rate of MgO ($mol\,m^{-2}\,s^{-1}$)
r_c	coefficient of correlation
R	gas constant = 8.314 ($J\,mol^{-1}\,K^{-1}$)
S	total surface area of the solid (m^2)
S.D.	standard deviation
t	time of leaching (s)
T	temperature (K)
V_R	volume of reaction mixture (dm^3)
X	fraction of MgO dissolved

Greek letters

ϑ	temperature (°C)

order n (frequently values in the range $0 < n < 0.6$ [5,6,18,20–24]) which is compatible with kinetic theories [6], or even indicative of a process controlled by surface reaction. However, in some cases there are situations when the application of different theoretical approaches results in identifying various potential rate-controlling steps for identical reaction conditions, with no clear basis for discrimination between these alternatives [3,27–29]. Furthermore, for the initial stage of the process of MgO dissolution in dilute acids [20] and for MgO dissolution using concentrated hydrochloric acid (pH < 1) [13,14], negative values of the reaction order for H^+ ions have been reported. A retardant effect of acid concentration on the dissolution rate is in conflict with the theories and, indeed, the evidence in the literature [5]. Progress towards an agreed understanding of all the phenomena involved comes through extensive and systematic experimental study of MgO dissolution behaviour in a wide range of reaction conditions.

Although the effect of anion might not be expected at low acid concentrations (≤0.01 M), there is some evidence that this needs not to be true. For example, higher rates of MgO dissolution were observed in HCl than in $HClO_4$ at pH 2.0–3.5 [20]. Furthermore, MgO dissolution rates measured by various authors [16,18,20–25] under various reaction conditions (periclase used – single crystal or polycrystalline, acid used – mostly HCl or HNO_3, pH) and using different experimental methods (chemical analysis of leachate or AFM) are generally different. The aim of this work is therefore to provide additional information on the dissolution kinetics of MgO. Unlike most other authors who have studied MgO single crystals [5,15–18,20,22–26], our experiments were performed using polycrystalline MgO. In contrast to the recent detailed study on kinetics of MgO dissolution in diluted HCl, focusing on the difference between the “initial” and “advanced” regime of dissolution [30], in the present work we investigate the “advanced” dissolution behaviour of periclase, with special regard to the effects of pH and the type of the inorganic acid used, especially HCl, HNO_3 and H_2SO_4. The effect of temperature was analysed as well, to extend the existing kinetic data following from the works of other authors (the reaction conditions used are shown in Fig. 1 in the context of the works of other authors).

2. Theoretical background

Chemical dissolution of MgO in acidic aqueous solutions is a liquid–solid reaction in which no solid product is formed. For non-porous periclase, the overall process may be controlled by the surface chemical reaction

$$MgO_{(s)} + 2H_{(aq)}{}^{+} \rightarrow Mg_{(aq)}{}^{2+} + H_2O_{(l)} \qquad (1)$$

or by external mass transfer [31,32]. The chemical reaction (1) involves the transfer of magnesium cations and oxygen anions from the solid to the solution in which the cations are hydrated. The transfer of anions involves protonation or hydroxylation reactions at the surface of the solid, forming water. No oxidation or reduction is required [5].

When MgO particles are dissolved in diluted acid characterized by the initial value of pH, pH^0, the total surface area of the solid, S, does not change significantly during the early stages of dissolution, and the pH–t relationship can be approximated using a simple expression

$$10^{-pH^0} - 10^{-pH} = \frac{2r'S}{V_R}t \qquad (2)$$

Eq. (2) is suitable for calculating the dissolution rate of MgO, r', using the measured pH–t data [30]; V_R is the volume of reaction mixture.

Kinetic theories of the dissolution of ionic oxides predict that the dissolution rate should have an inverse exponential dependence on solution pH [3,5,6,27,33,34]. The slope of a plot of log (rate) against pH is expected to depend either upon the particular reaction between protons and ionic oxygen-containing species at the oxide surface, or on the effect of the potential difference between oxide and solution on cationic and anionic species [20]. There are three different reactions of the surface anions with protons which

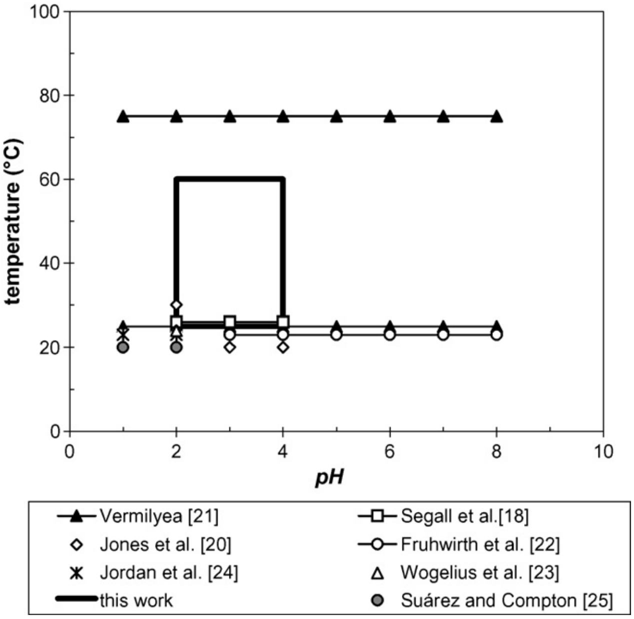

Fig. 1. Reaction conditions under which the chemical dissolution of MgO was studied in the present work, compared with those referred to in the literature.

Table 1
Possible rate-determining steps for MgO dissolution and theoretical predictions of the corresponding slopes of log (rate) against pH dependence

Slope ($-n$)	Rate-determining step	Author of the theory	Literature
0	Reaction (3) – anion-removal control	Diggle	[5,6,28]
−1/2	Reaction (3)	Vermilyea	[5,6,27]
	Reaction (4) – anion-removal control	Diggle	[5,6,28]
	Proton adsorption and slow penetration of the solid phase	Gorichev and Kyprianov	[3,5]
−2/3	Reaction (4)	Vermilyea	[5,6,27]
−1	Cation removal control for whichever of the reactions (3), (4) or (5)	Diggle	[5,6,28]
	Reaction (5) – anion-removal control		
	Reaction (5)	Vermilyea	[5,6,27]
	Diffusion through the liquid film at the liquid–solid interface		

may control the overall rate of the reaction (1):

$$\equiv|\mathrm{Mg}=\mathrm{O}+\mathrm{H}^+ \rightarrow \mathrm{Mg}^{2+}+\mathrm{OH}^-, \tag{3}$$

$$\equiv|\mathrm{Mg}-\mathrm{OH}^+ +\mathrm{H}^+ \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_2\mathrm{O}, \tag{4}$$

$$\equiv|\mathrm{Mg}=\mathrm{O}+2\mathrm{H}^+ \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_2\mathrm{O}. \tag{5}$$

Values of the slope ranging between −1 and 0 are generally predicted for MgO by theoretical kinetic models—Table 1.

3. Experimental procedure

3.1. Materials

Bulk high-grade synthetic polycrystalline periclase HAMAG 99.5 made from magnesite from Hačava, Slovakia was used in the present study. Size fractions were obtained by short dry-milling and dry-screening. To eliminate the effect of very small particles adjacent to the surface of larger ones, the fractions were washed on screens with acetone, dried and dry-screened again. The physico-chemical characteristics of the samples used for the leaching experiments (and named HAM/mean particle diameter) are given in Table 2. The solid samples were analysed using the AAS method, and the specific surface area was determined using the BET nitrogen adsorption technique. Since the total amount of impurities (i.e. CaO, Fe_2O_3, Al_2O_3 and SiO_2) was very low, mineralogical composition was predicted from phase equilibrium relationships [35]; it seems likely that the periclase (99.6 wt.%) was accompanied by dicalciumsilicate, brownmillerite, magnesioferrite and dicalciumferrite. Presence of periclase as the predominant mineral phase was verified using X-ray diffraction analysis. Analytical reagent grade chemicals and distilled water were used in all experiments.

3.2. Experimental procedure and measuring kinetic data

Dissolution of the samples of periclase was tested in a 1.1 L isothermal well-mixed glass batch reactor with a six-blade turbine impeller, four baffles installed, and a thermometer. The temperature was maintained to within 0.2 K by a heating glass coil connected to a thermostat.

The dissolution rates of a known initial mass of solid in dilute acid solutions were determined by recording the solution pH as a function of time. In all cases, 800 mL of lixiviant (diluted HCl, HNO_3 or H_2SO_4) were placed in the reactor. When the solution reached the required temperature, the accurate initial value of pH was adjusted and an appropriate amount of MgO was added (1000, 100 or 10 mg of MgO were dissolved at pH^0 equal to 2, 3 and 4, respectively). The electrode was calibrated before each series of experiments using standard buffer solutions.

The experiments were carried out under reaction conditions as follows: temperature from 25 to 60 °C and concentration of mineral acid from 10^{-4} to 10^{-2} M. In each of the experiments, at least three runs were made for a given set of reaction conditions and pH^0 and initial mass of MgO.

Table 2
Physico-chemical characteristics of samples of periclase

	Sample		
	HAM/67	HAM/113	HAM/335
(1) Particle diameter (μm)	63–71	100–125	315–355
(2) Mean particle diameter (μm)	67	113	335
(3) Specific surface area ($m^2 g^{-1}$)	0.11	0.09	0.02
(4) Chemical composition (wt.%):			
MgO		99.6	
CaO		0.15	
Fe_2O_3		0.12	
Al_2O_3		0.02	
SiO_2		0.04	
L.O.I.		<0.1	

4. Results

In this section, the results are presented in terms of the fraction of MgO dissolved, X, plotted against reaction time t, which seem to be more illustrative than the original pH–t data. Measured values of

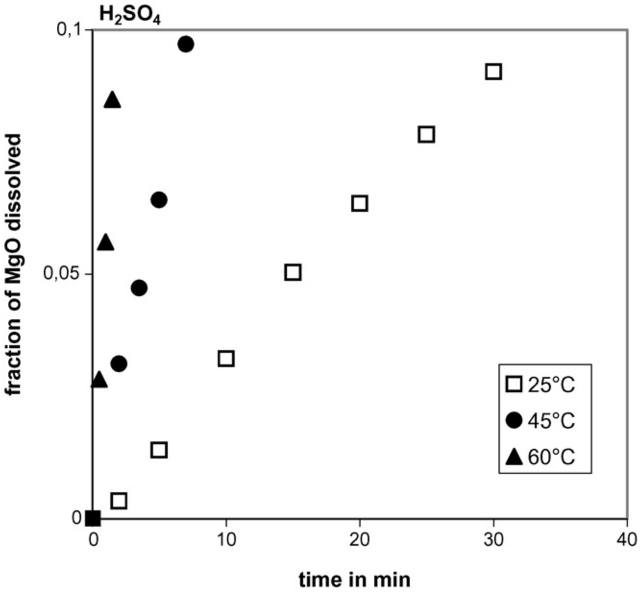

Fig. 2. Effect of temperature on fraction of MgO dissolved (reaction conditions: sample HAM/113 dissolved in H_2SO_4 at $pH^0 = 2.0$).

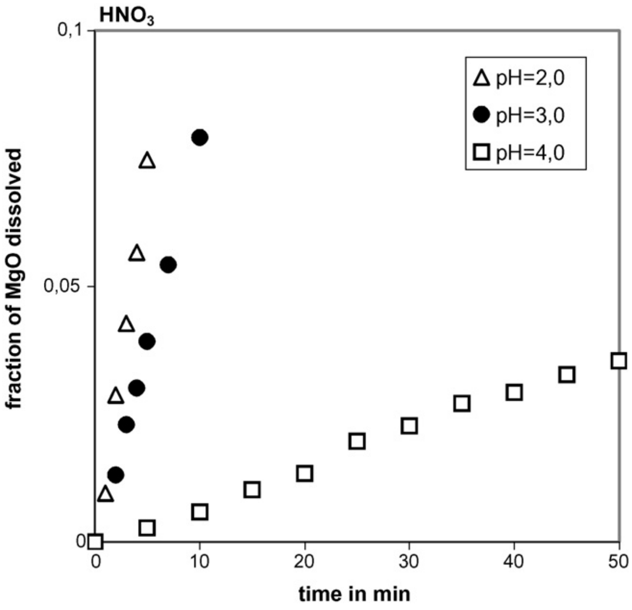

Fig. 3. Effect of acid concentration on fraction of MgO dissolved (reaction conditions: sample HAM/113 dissolved in HNO_3 at $\vartheta = 45\,^\circ C$).

pH were converted to corresponding X values using the expression

$$10^{-\mathrm{pH}^0} - 10^{-\mathrm{pH}} = \frac{2m^0_{\mathrm{MgO}}}{V_{\mathrm{R}} M_{\mathrm{MgO}}} X, \tag{6}$$

where m^0_{MgO} is the initial amount of MgO in mass units; M_{MgO} the mole mass of MgO ($M_{\mathrm{MgO}} = 40.3\,\mathrm{g\,mol^{-1}}$) [30].

4.1. *Effect of temperature*

The temperature dependence of the dissolution rate was determined for the fraction 100–125 μm in HCl, HNO_3 and H_2SO_4 for initial values of pH equal to 2, 3 and 4, at solution temperatures of 25, 45 and 60 °C. A typical situation is shown in Fig. 2. It can be seen that the rate of MgO dissolution is very sensitive to the temperature.

4.2. *Effect of acid concentration*

The effect of acid concentration (pH) was studied through a series of tests performed at 25, 45 and 60 °C using HCl, HNO_3 and H_2SO_4 solutions with initial pH values 2, 3 and 4. The experiments showed that the rate of transfer of magnesium to the solution is significantly affected by pH; a typical example is presented in Fig. 3.

5. Discussion

5.1. *Experimental method*

We have shown in our previous work [13,14,30] that the dissolution behaviour of periclase can be described using the shrinking particle model (SPM) in a wide range of temperatures and concentrations of H^+ ions. For $X < 0.1$, the actual X–t dependence can be approximated by a linear equation with a relative error of less than 4%, which was used to choose an appropriate liquid-to-solid ratio for individual runs [30].

5.2. *Rate of dissolution*

The dissolution rates were obtained for individual runs by linearised regression using Eq. (2). Only the data represented by linear

Table 3
Rates of MgO dissolution obtained by regression of measured data

Temperature (°C)	pH^0	r' in $10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}}$	$\log r'$		
			$\log \overline{r'}$	$\log(\overline{r'} - \mathrm{S.D.})$	$\log(\overline{r'} + \mathrm{S.D.})$
(a) For HCl					
25	2.0	15.7 ± 0.4	−4.805	−4.816	−4.794
	3.0	6.40 ± 0.33	−5.194	−5.217	−5.172
	4.0	2.23 ± 0.10	−5.652	−5.672	−5.632
45	2.0	76.9 ± 1.2	−4.114	−4.121	−4.108
	3.0	21.7 ± 2.0	−4.664	−4.707	−4.625
	4.0	4.14 ± 0.22	−5.383	−5.407	−5.360
60	2.0	171 ± 3	−3.767	−3.774	−3.760
	3.0	39.1 ± 3.9	−4.408	−4.453	−4.367
	4.0	4.87 ± 0.14	−5.312	−5.325	−5.300
(b) For HNO_3					
25	2.0	15.83 ± 0.22	−4.801	−4.807	−4.795
	3.0	6.66 ± 0.34	−5.177	−5.200	−5.155
	4.0	2.80 ± 0.09	−5.553	−5.567	−5.539
45	2.0	84.36 ± 2.12	−4.074	−4.085	−4.063
	3.0	17.23 ± 1.66	−4.764	−4.808	−4.724
	4.0	3.52 ± 0.12	−5.454	−5.469	−5.438
60	2.0	217 ± 4.86	−3.663	−3.673	−3.654
	3.0	35.09 ± 4.51	−4.455	−4.514	−4.402
	4.0	5.67 ± 0.35	−5.246	−5.274	−5.220
(c) For H_2SO_4					
25	2.0	17.90 ± 0.34	−4.747	−4.755	−4.739
	3.0	10.37 ± 0.32	−4.984	−4.998	−4.971
	4.0	6.01 ± 0.10	−5.221	−5.221	−5.221
45	2.0	65.29 ± 3.03	−4.185	−4.206	−4.166
	3.0	19.02 ± 1.21	−4.721	−4.749	−4.694
	4.0	5.54 ± 0.23	−5.256	−5.275	−5.238
60	2.0	294.6 ± 6.62	−3.531	−3.541	−3.521
	3.0	38.62 ± 11.18	−4.413	−4.562	−4.303
	4.0	5.06 ± 0.55	−5.296	−5.345	−5.251

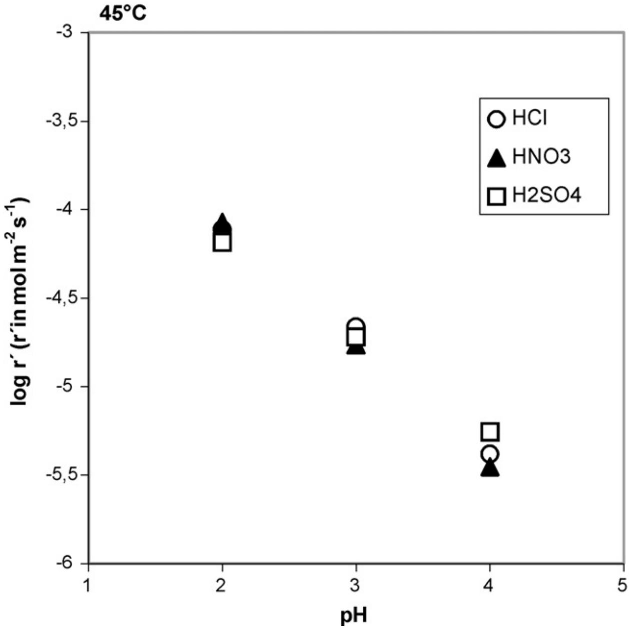

Fig. 4. Effect of the type of inorganic acid used on the dependence of log (rate) vs. pH^0 (reaction conditions: sample HAM/113 at $\vartheta = 45$ °C).

segments of the X–t plots were considered, and the results are summarized in Table 3.

To compare our results with the theory, we plotted the values of log (rate) against pH—a typical situation is presented in Fig. 4.

From Fig. 4 it can be seen that the dependence of log r' on pH is linear and practically identical for all three acids used, allowing for experimental error, under the conditions of the experiments in the present work.

Comparing the data in Table 3, there might be some evidence for higher dissolution rates in sulphuric acid at pH 2, especially at 60 °C. Useful information for further discussion can be obtained from E–pH diagrams of the systems S–H_2O and Mg–S–H_2O. The first diagram shows that sulphuric acid can be expected to behave as a monobasic acid because HSO_4^- ions prevail in the solution of H_2SO_4 at temperatures 25–60 °C and pH 2. The second one indicates that while Mg^{2+} cations may form ion pairs with SO_4^{2-} anions at temperature 25 °C and pH ≈ 2, this seems not to be true at higher temperatures (because the left border of $MgSO_4$ stability region is shifted to higher pH values). The enhancement of MgO dissolution due to increased H^+ concentration resulting from $MgSO_4$ ion-pairs formation and subsequent HSO_4^- dissociation in solution seems to be therefore unlikely. Furthermore, the increase of H^+ concentration due to HSO_4^- dissociation could partially counterbalance the increase in pH due to MgO dissolution, which would result in lower measured dissolution rates. Considering these facts, as well as the differences between other values of dissolution rates in Table 3, we conclude that no significant enhancement of MgO dissolution in H_2SO_4 solutions has been observed.

Table 5
Experimental values of the slopes of log (rate) vs. pH obtained by linearised regression of measured log r'–pH^0 data using Eq. (7)

Temperature (°C)	Slope ($-n$)		
	HCl	HNO_3	H_2SO_4
25	−0.41 ± 0.10	−0.38 ± 0.17	−0.24 ± 0.36
45	−0.62 ± 0.26	−0.69 ± 0.19	−0.54 ± 0.23
60	−0.76 ± 0.31	−0.79 ± 0.29	−0.88 ± 0.29

The variation in both our and published rates for MgO at 25 °C for pH between 2 and 4 is shown in Table 4.

The data presented in Table 4 indicate that the values of dissolution rates may differ significantly. Considerably higher rates reported by Vermilyea [21] and Fruhwirth et al. [22] are most likely due to the usual problems of surface area normalization (the rates reported by Vermilyea [21] and Fruhwirth et al. [22] are related to the geometrical area assuming smooth surfaces, while those measured by other authors [18,23–25] are related to the active surface area determined by gas adsorption). Other differences between the experiments probably include the use of KCl [21,22] to stabilize the solution potential.

In spite of the difference in dissolution rates observed in general, there is a very good correlation between the present values and those obtained by other authors when normalized to the B.E.T. surface area of MgO (Segall et al. [18], Wogelius et al. [23], Jordan et al. [24] and Suárez and Compton [25]).

5.3. *Mechanism of dissolution*

To estimate the degree of interaction between the surface chemical reaction (1) and external mass transfer, the mass transfer coefficient k_{LS} was calculated by method recommended in the literature [32]. For example, the values of k_{LS} equal to $(0.4–0.6) \times 10^{-3}\,m\,s^{-1}$, $(0.7–1.0) \times 10^{-3}\,m\,s^{-1}$ and $(1.0–1.3) \times 10^{-3}\,m\,s^{-1}$ were obtained for HCl at 25, 45 and 60 °C, respectively. These estimates of k_{LS} were used to calculate the logarithms of corresponding diffusion rates of HCl (in mol $m^{-2}\,s^{-1}$) for pH between 2 and 4 and the following results were obtained: −2.176 to −4.217 at 25 °C, −1.976 to −4.017 at 45 °C and −1.840 to −3.881 at 60 °C. Since the calculated diffusion rates were found to be almost by two orders of magnitude higher than the measured overall reaction rates (see Table 3), we conclude that the rate-controlling step of MgO dissolution was the surface chemical reaction (1). Analogical procedure was used to analyse the effect of diffusion on the overall process of MgO dissolution in HNO_3 and H_2SO_4.

Table 4
Rates of chemical dissolution of MgO (expressed as log r', r' in mol $m^{-2}\,s^{-1}$) at 25 °C obtained in the present work, compared with those reported in the literature

pH						
2				3		4
−4.04 [21]; HCl				−4.11 [21]; HCl		–
				−4.45 [22]; HCl		−4.39 [21]; HCl
−4.72 [25]; HCl	−4.75; H_2SO_4	−4.80; HNO_3	−4.81; HCl			
−5.02 [18]; HNO_3				−4.98; H_2SO_4		−5.09 [22]; HCl
−5.14 [23]; HNO_3				−5.18; HNO_3	−5.19; HCl	−5.22; H_2SO_4
−5.25 [24]; HCl						−5.35 [22]; HCl
				−5.52 [18]; HNO_3		−5.55; HNO_3
						−5.65; HCl
						−5.82 [23]; HNO_3
						−5.98 [18]; HNO_3

Table 6
Experimental values of apparent activation energy

	pH^0								
	2.0			3.0			4.0		
	HCl	HNO_3	H_2SO_4	HCl	HNO_3	H_2SO_4	HCl	HNO_3	H_2SO_4
E (kJ mol^{-1})	93 ± 2	104 ± 9	120 ± 12	101 ± 7	122 ± 2	147 ± 11	96 ± 3	104 ± 9	180 ± 11
r_c^2 (−)	0.996	0.970	0.971	0.978	0.999	0.988	0.995	0.972	0.984
N (−)	8	6	5	6	4	4	6	6	6

The heat-transfer coefficient for the transfer of heat through the liquid film at the surface of solid particles was estimated, as well. The values higher than $2 \times 10^4\,\mathrm{J\,m^{-2}\,s^{-1}\,K^{-1}}$ were calculated for HCl, which indicates that the dissolution was practically isothermal (the increase in MgO particle surface temperature due to the heat generated by chemical reactions was found to be less than 0.01 K). We therefore conclude that the surface chemical reaction (1) practically took place at the temperature of the bulk liquid under the conditions considered in the present work.

The rate r' of reaction (1) can be expressed as a power-law function of the activity of H^+ ions on the particle surface, a_{H^+w},

$$r' = k_S a^n_{H^+w}. \tag{7}$$

The coefficient k_S is the apparent reaction-rate constant and n is the apparent order of the overall surface chemical reaction (1); $-n$ being the slope of the plot of log (rate) against pH.

Temperature dependence of k_S can be expressed using the Arrhenius expression

$$k_S = k_0 \exp\left(\frac{-E}{RT}\right), \tag{8}$$

where k_0 is the frequency factor; E the apparent energy of activation; R the gas constant.

The values of parameters n and E were obtained by linearised regression using Eqs. (7) and (8), respectively, and are summarized in Tables 5 and 6. The fractional reaction order for H^+ ions and high activation energy are indicative of a process controlled by surface reaction.

The 95% confidence limits for the slopes of log (rate) vs. pH^0 at various temperatures obtained by linearised regression are shown in Fig. 5a–c.

It can be seen from Fig. 5a–c that the 95% confidence limits for the slopes ($-n$) obtained for dissolution in HCl, HNO_3 and H_2SO_4 at the same temperature overlap. That indicates that no significant

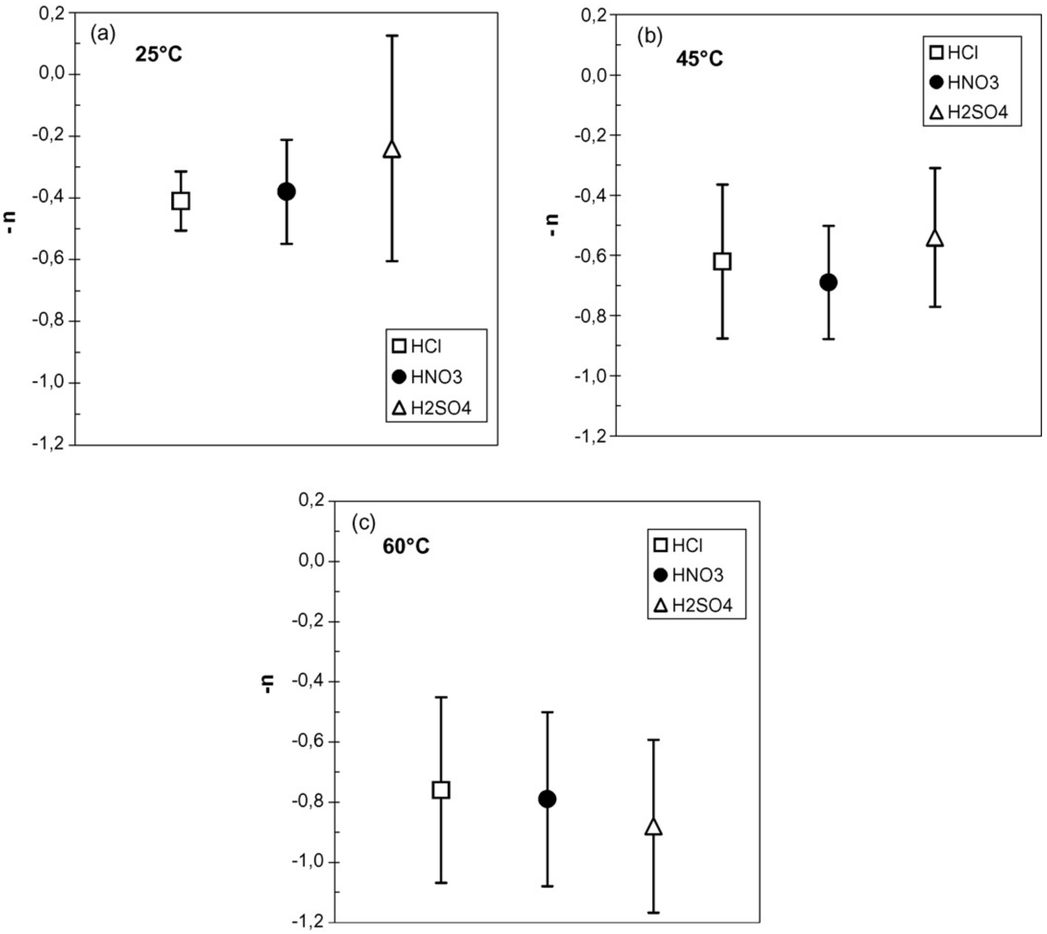

Fig. 5. 95% confidence limits for calculated values of the slopes of log (rate) vs. pH^0 at various temperatures: (a) 25 °C; (b) 45 °C; and (c) 60 °C.

effect of acid anion on the dissolution rate of MgO was detected under the conditions of the present work.

The slope of the plot of log (rate) against pH was used to identify the rate-determining step of the overall process of MgO dissolution. The likely rate-determining steps for various reaction conditions were determined by comparing the data in Table 5 with "theoretical" values summarized in Table 1.

Even though our slopes are consistent, allowing for experimental error, with current theories, in some cases the rate-controlling step could not be assigned unambiguously for two main reasons. Firstly, the same value of the reaction order for H^+ ions can be predicted by various theories for different rate-determining steps—the situation is illustrated in Table 1. Secondly, in some cases, the experimental value of the slope (or rather the 95% confidence limits for the slope) cannot be assigned to the unique theoretical value, due to experimental error.

At 25 °C, the experiments showed linear dependence of log (rate) on pH, with a slope ranging from -0.24 ± 0.36 to -0.41 ± 0.10. Despite similar results to ours in the literature, the situation is ambiguous. According to the theories of dissolution of divalent oxides based on removal of oxide or hydroxide ions by reaction with protons [27,28] this dependence is consistent with either anion-removal control via the protonation of O^{2-} to OH^- (reaction (3) [27,28]) or anion-removal control via OH^- to H_2O (reaction (4) [28]. On the other hand, proton adsorption and slow penetration of the solid phase [3] also appears to be a possible rate-determining step—see Table 1. In the light of the fast protonation not only of the surface but also of the near-surface region [23,24], reaction (3) is unlikely to be the rate-determining step. We expect that, under "advanced" regime conditions, the MgO dissolution can be controlled by the second protonation (reaction (4)).

At higher temperatures, anion-removal for reaction (3) or (4), or cation removal for whichever of the reactions (3)–(5)) should be considered as a potential rate-determining step. However, the second protonation reaction (4) seems to play the most important role.

Although the reaction order *n* seems not to be affected by the type of acid used, the apparent activation energies in Table 6 change in the order $HCl \leq HNO_3 < H_2SO_4$. Higher values of activation energy obtained for H_2SO_4 could therefore indicate that the chemical dissolution of MgO according to Eq. (1) is controlled by different reactions between the surface anions and protons liberated from H_2SO_4 and HCl (or HNO_3), Eqs. (3)–(5). This difference in mechanism could be attributed to the differences in complexing powers of sulphate and chloride (or nitrate) anions with Mg^{2+} cations; because the values of formation constants of $MgSO_4$(aq) and $MgCl^+$(aq) are 10.2–169.8 and 0.1–0.79, respectively, depending on the ionic strength of the solution at 25 °C [36,37].

6. Conclusions

The kinetics of the dissolution of sintered polycrystalline periclase in hydrochloric acid (HCl), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) under *advanced* kinetic regime conditions were studied. Several features indicate that the dissolution is controlled by the chemical reaction of MgO with H^+ ions at the liquid–solid interface:

1. The measured dissolution rates being by up to two orders of magnitude lower than the rate of external mass transfer.
2. High values of apparent activation energy.
3. Fractional reaction order for H^+ ions.

Thorough comparison of our dissolution rates with those published in the literature reveals that there is a very good correlation between the present values and those measured by the other authors when normalized to the B.E.T. surface area of MgO. Even though our slopes of log (rate) against pH are consistent, allowing for experimental error, with current theories, the rate-controlling step could not be assigned unambiguously, because in some cases the experimental value of the slope (or rather the 95% confidence limits for the slope) cannot be assigned to the unique rate-determining step.

Measured values of the reaction order for H^+ ions are indicative that the rate is limited by the second protonation reaction, i.e. the slow reaction of surface hydroxide with a second proton. Though the reaction order *n* for H^+ ions seems not to be affected by the type of acid used, the apparent activation energy changes in the order $HCl \leq HNO_3 < H_2SO_4$. Higher values of activation energy obtained for H_2SO_4 could indicate that surface chemical reaction is controlled by different reactions between surface anions and protons created by dissociation of H_2SO_4 and HCl (or HNO_3).

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