

## DISSOLUTION KINETICS OF SEPIOLITE FROM ESKISEHIR (TURKEY) IN HYDROCHLORIC AND NITRIC ACIDS

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**ABSTRACT:** Dissolution kinetics of sepiolite from Eskisehir (Turkey) have been investigated at various temperatures and particle sizes using dilute hydrochloric and nitric acids. Dissolution reaction rate constants were calculated and apparent activation energies were dependent on acid concentration. For both acids, apparent activation energy values reached a minimum of ~11 kcal/mol at an acid concentration of 0.75 M. For the second-order reaction which is independent of the acid concentration, the activation energy was 14.5 kcal/mol for both acids. The reaction rate constants were proportional to the acid concentrations, and inversely proportional to the square-root of the initial particle radii of the sepiolite.

The activation of natural clay surfaces by acid treatment has been studied extensively. Dissolution of Mg from sepiolite mined at Eskisehir (Turkey) using dilute acids was first attempted by Abdul-Latif & Weaver (1969) who found that dissolution of palygorskite and sepiolite in excess hydrochloric acid was a first order reaction in terms of concentrations of Al, Fe and Mg. They also noticed that the dissolution reaction rate constant of Mg in sepiolite was 240 times that for Mg in palygorskite.

Several studies of the acid activation of Spanish sepiolite have been carried out to improve the surface area and porosity (Jimenez-Lopez *et al.*, 1978; Rodriguez-Reinoso *et al.*, 1981) and the amount of the surface acidity (Bonilla *et al.*, 1981), to determine the structural changes in the sepiolite (Shimosaka *et al.*, 1973; Corma *et al.*, 1986) and to obtain good quality products for use as adsorbents (Gonzalez *et al.*, 1984), filling materials (Gonzalez *et al.*, 1982; Acosta *et al.*, 1984) and catalysts (Dandy & Nadiye-Tabbiruka, 1982; Corma *et al.*, 1984; Corma & Perez-Pariente, 1987). In these studies, activation was performed in hydrochloric and nitric acids of various concentrations, the temperature being varied to obtain the most suitable conditions for a specific purpose. It was observed that in acid solutions with a concentration >1 M, the sepiolite structure collapsed and amorphous silica was formed when practically all the Mg went into solution. An activated product of maximum surface area and surface acidity was obtained with an acid solution of 0.75 M concentration.

The activation energies associated with the dissolution of the  $\text{Mg}^{2+}$  ion from sepiolite were found to be 15.13 kcal/mol and 14.91 kcal/mol in 2 M and 6 M HCl, respectively (Gonzalez *et al.*, 1984). This activation energy was reported to be 21.5 kcal/mol in 1 M HCl (Corma *et al.*, 1986) and 14.72 kcal/mol and 14.35 kcal/mol in 3 M and 6 M  $\text{HNO}_3$ , respectively (Gonzalez *et al.*, 1982).

In this study, dilute HCl and  $\text{HNO}_3$  of varying concentrations were employed at various

temperatures and with different particle sizes to investigate the dependence of the dissolution of the  $\text{Mg}^{2+}$  ions on these parameters. The reaction rate constant and the activation energy were calculated by a least-squares graphical method.

## MATERIAL AND METHODS

The sepiolite mineral used is from Eskisehir with the following composition:  $\text{SiO}_2$  56.91%,  $\text{MgO}$  27.52%,  $\text{Al}_2\text{O}_3$  0.09%,  $\text{Fe}_2\text{O}_3$  0.04%,  $\text{CaO}$  1.40%,  $\text{TiO}_2$  0.01%,  $\text{Na}_2\text{O}$  0.02%,  $\text{K}_2\text{O}$  0.01% and loss-on-ignition 14.00% (Cetisli, 1988, 1989).

The reactions were carried out in a batch-type heater-jacketed reactor of 150 ml capacity, using 0.50 g of sepiolite and 100 ml of acid solution. The reactor was kept at the desired temperatures by circulating water from a constant temperature bath, and a mechanical stirrer was used for constant stirring. The concentration of  $\text{Mg}^{2+}$  extracted into the solution was determined in representative portions of solutions taken at regular intervals. Complexometric titration was employed to determine the concentration of  $\text{Mg}^{2+}$  using an EDTA solution and Indikator-Puffertabletten as indicator (Gülensoy, 1984).

Hydrochloric and nitric acids were used at 23°C, 33°C and 54°C at concentrations of 0.25, 0.50, 0.75, 1.00 and 2.00 M, the particle size of the sepiolite being 170–200 mesh (0.081 mm average). To investigate the effect of particle size on the dissolution rate, three particle size fractions were treated with 0.75 M acids at 33°C: 25–50 mesh (average 0.5020 mm), 50–70 mesh (average 0.2535 mm) and 70–100 mesh (average 0.1795 mm).

## RESULTS

The kinetics of solid-liquid heterogenous reactions are quite complex due to the change of the interface upon which the reaction takes place, and also the change in the surface area of the solid resulting from the diffusion effects of various extent. It has been established by Abdul-Latif & Weaver (1969) that dissolution of  $\text{Mg}^{2+}$  from sepiolite was a first order reaction in terms of the acid concentration and the  $\text{Mg}^{2+}$  content. It has also been shown that in excess acid medium, if the dissolved layer of the cylindrical particle acts as a barrier to further diffusion, the kinetics of the dissolution reaction obey the following rate equation (Wadworth & Miller, 1979; Gonzalez *et al.*, 1982; Gonzalez *et al.*, 1984; Corma *et al.*, 1986; Cetisli, 1988):

$$[1 - (1 - \alpha)^{\frac{1}{2}}]^2 = \frac{2k'}{r^2} t = k t$$

$\alpha$  denotes the ratio of the amount of Mg taken into solution in  $t$  seconds to the initial total content of Mg,  $k$  and  $k'$  are the reaction rate constants,  $r$  is the initial radius of the sepiolite particle, and  $t$  is time elapsed. The specific rate-constant  $k$  is a function of temperature, acid concentration, particle size, number of active sites on the solid, and the diffusion constant. As sepiolite samples with identical properties were used in all the experiments, the rate constant was considered to be expressed as a function of temperature, acid concentration, and particle size.

The values  $[1 - (1 - \alpha)^{\frac{1}{2}}]^2$  were plotted against time  $t$  to verify the validity of the tentative equation given above. As can be seen in Figs. 1, 2 and 3, all the experimental values plot on straight lines, indicating that the theoretical model works well in this case. The  $k$  values calculated from the slopes of the straight lines together with the acid concentrations and the reaction temperatures are given in Table 1.

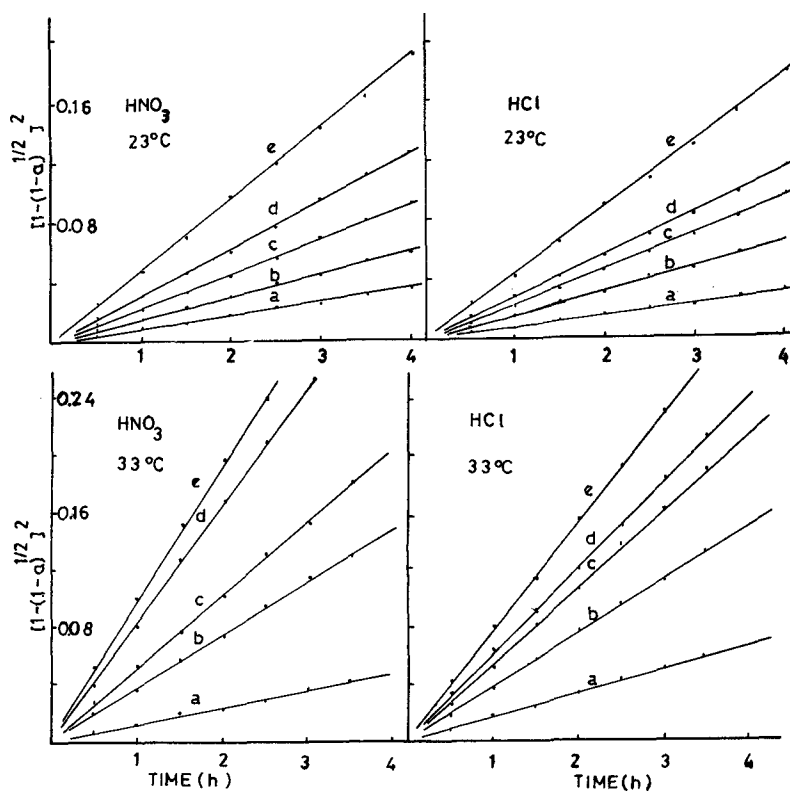


FIG. 1. Straight lines relating to the kinetics of dissolution of Mg from sepiolite in  $\text{HNO}_3$  and  $\text{HCl}$  solutions. a: 0.25 M; b: 0.50 M; c: 0.75 M; d: 1.00 M; e: 2.00 M.

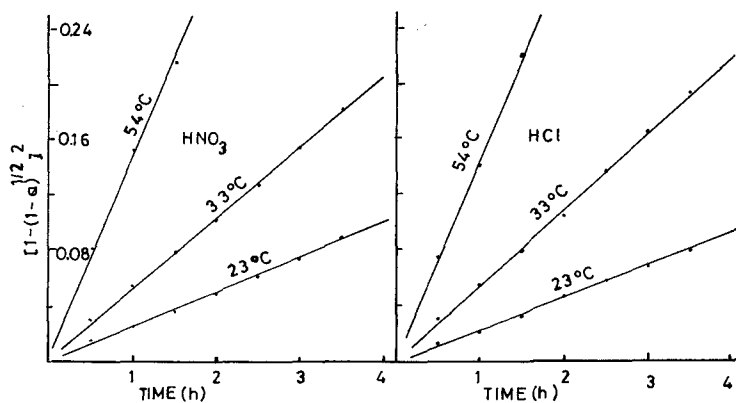


FIG. 2. Straight lines relating to the kinetics of dissolution of Mg from sepiolite in 0.75 M  $\text{HNO}_3$  and 0.75 M  $\text{HCl}$ .

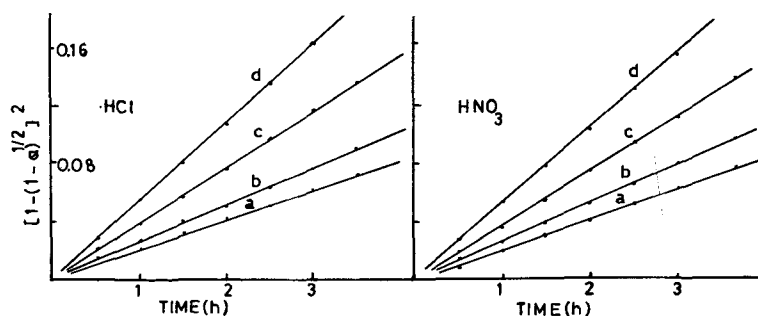


FIG. 3. The effect of particle size on the kinetics of the dissolution reaction of Mg from sepiolite at 306.15 K and 0.75 M acid. Particle diameters—a: 0.5020 mm; b: 0.2535 mm; c: 0.1795 mm; d: 0.0810 mm.

TABLE 1. Dissolution reaction rate constants relating to the extraction of Mg from sepiolite ( $k \times 10^4 \text{ min}^{-1}$ ).

Type of acid	T°K	Acid concentration (mol/l)				
		0.25	0.50	0.75	1.00	2.00
HCl	296.15	1.128	2.568	3.867	3.905	7.500
	306.15	2.878	6.195	8.947	9.554	11.920
	327.15	11.070	19.102	23.992	42.767	90.018
HNO <sub>3</sub>	296.15	1.625	2.226	4.039	5.364	8.288
	306.15	2.076	7.419	8.575	14.768	15.855
	327.15	12.733	17.512	24.326	44.318	99.569

TABLE 2. Values of the apparent activation energies for different acids and acid concentrations ( $E_a$  kcal/mol).

Type of acid		Acid concentration (mol/l)				
		0.25	0.50	0.75	1.00	2.00
HNO <sub>3</sub>		13.365	12.196	10.983	12.758	15.698
HCl		13.994	12.226	11.101	14.458	15.923

TABLE 3. Numerical values of  $n$  and  $k'$  ( $\text{min}^{-1}$ ) calculated from experimental values of  $k$  ( $k = k' \cdot C^n$ ).

T°K	HCl		HNO <sub>3</sub>	
	$n$	$k' \times 10^4$	$n$	$k' \times 10^4$
296.15	0.884	4.279	0.834	4.827
306.15	0.982	8.935	0.980	10.979
327.15	1.011	39.902	1.018	42.054

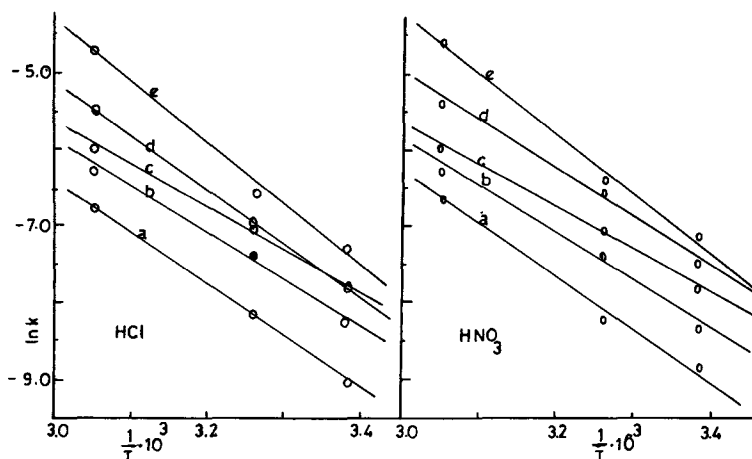


FIG. 4. Arrhenius plots relating to the dissolution of Mg in sepiolite. a: 0.25 M; b: 0.50 M; c: 0.75 M; d: 1.00 M; e: 2.00 M.

Considering the validity of the Arrhenius Equation  $k = A e^{-Ea/RT}$  the  $\ln k$  values obtained with the same acid treatment at different temperatures were plotted against  $1/T$  (Fig. 4). The straight lines are quite close to the intrinsic case. The apparent activation energies were calculated from the slopes of these lines (Satterfield, 1980), and the  $Ea$  values for the different concentrations of acids are given in Table 2.

When the particle size of the sepiolite and the reaction temperature were kept constant, rate constants become proportional to the acid concentrations. Considering the basic equation  $k = k' \cdot C^n$ ,  $\ln k$  values were plotted against  $\ln C$  (Fig. 5), and the slopes of the lines give the  $n$  values, whereas the intercepts correspond to  $k'$ . The  $n$  and  $k'$  values calculated in this way are given in Table 3.

The dissolution reactions in 0.75 M acids at 33°C were carried out using four different particle sizes, with the other parameters remaining unchanged. The plots of  $[1 - (1 - \alpha)^{1/2}]^2$  vs. time for these reactions are shown in Fig. 3 and the rate constants calculated from the slopes of these lines are given in Table 4.

As the calculated rate constants are a function of the initial particle radii, the equation  $k = k'/r^x$  is taken as a trial function, and  $\ln k$  was plotted vs.  $\ln r$  (Fig. 6). From the slope of the straight line so obtained, an average numerical value of +0.5350 was calculated for the parameter  $x$  (+0.5583 for HCl, and +0.5115 for HNO<sub>3</sub>).

TABLE 4. Change of the rate constant with particle size for the dissolution reaction of Mg from sepiolite at 306.15°K and in 0.75 M acids ( $k \times 10^4 \text{ min}^{-1}$ ).

Type of acid	Particle size ( $\theta$ mm)			
	0.5020	0.2535	0.1795	0.0810
HNO <sub>3</sub>	3.492	4.334	6.143	8.575
HCl	3.393	4.118	6.364	8.947

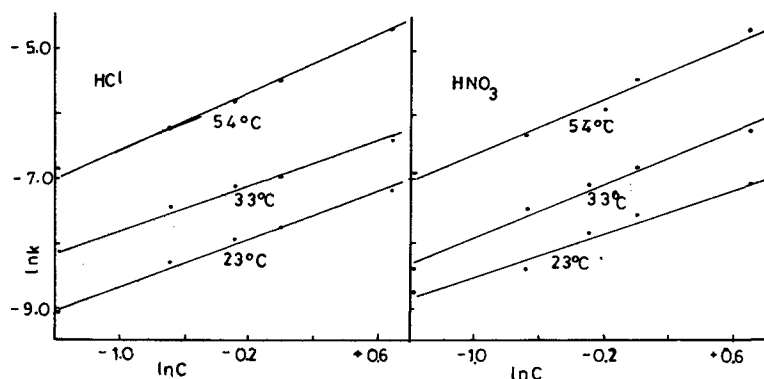


Fig. 5. Change of the rate constant ( $k$ ) with acid concentration.

The amounts of Mg extracted in three hours at various acid concentrations and temperatures in the conditions described in the material and methods section are tabulated in Table 5.

## DISCUSSION

As is evident from Figs. 1, 2 and 3, the dissolution of the  $\text{Mg}^{2+}$  ion in Eskisehir sepiolite proceeds by a kinetic model developed for the dissolution reactions of natural clay minerals. Tetrahedral silica sheets in the sepiolite structure and also formed as a result of the dissolution of the  $\text{Mg}^{2+}$  ion act as a diffusion barrier.

It is observed that the rate constants are proportional to the concentrations of both the acids, and the relationship between the acid concentration and the rate constant is linear (Fig. 5 and Table 3). The dissolution reaction of Mg from sepiolite is a first order one in terms of the Mg content in the solid and also the acid concentration.

The rate of the dissolution reaction of Mg increases as the temperature increases (Figs. 1, 2 and Table 1). The dependence of the rate constant on the temperature is more pronounced when the apparent activation energy is large, compared to the case where the apparent activation energy is small. The increase in the amount of dissolved  $\text{Mg}(\alpha)$  due to the increase in temperature appears to be greater compared to the treatment where the acid concentration was increased (Table 5), and this effect is more pronounced when the acid concentrations are low.

TABLE 5. Amount of Mg(%) extracted into solutions of HCl and  $\text{HNO}_3$  in three hours.

Reac. temp. $T^\circ\text{C}$	Acids concentrations (mol/l)									
	HCl					$\text{HNO}_3$				
	0.25	0.50	0.75	1.00	2.00	0.25	0.50	0.75	1.00	2.00
23	26.5	38.4	45.7	47.0	59.0	32.3	37.7	47.0	52.7	61.0
33	40.2	55.7	64.0	66.7	71.6	38.0	58.5	62.8	77.7	78.2
54	68.9	83.9	88.3	97.9	—	78.9	80.8	88.6	95.9	—

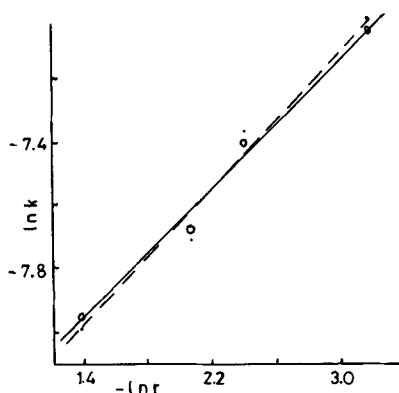


FIG. 6. Change of the rate constant with the initial particle radii. ---- for HCl, — for  $\text{HNO}_3$ .

The apparent activation energies calculated from Arrhenius' Equation were found to be dependent upon the acid concentration, and to reach a minimum at a concentration of 0.75 M (Table 2). The fact that the apparent activation energies were higher at concentrations higher or lower than this critical concentration is attributed to the diffusion effect. The diffusion rate of the hydronium ion from the solution to the active sites on the solid, as well as the diffusion rate of  $\text{Mg}^{2+}$  ions in the opposite direction, increases as the acid concentration increases. But an opposite process, namely formation of a tetrahedral silica layer which acts as a barrier to diffusion, counteracts the increase of the diffusion rate due to the increase in the acid concentration. Therefore the minimum value for the apparent activation energy appears to be the best compromise between the two competing factors. It has been reported that as the concentration of the acid used for the activation of sepiolite minerals increases, the porosity, pore volume and total surface area increase, and that new micro- and meso-pores that are more resistant to environmental effects are produced (Jimenez-Lopez *et al.*, 1978; Rodriguez-Reinoso *et al.*, 1981; Bonilla *et al.*, 1981; Gonzalez *et al.*, 1982; Gonzalez *et al.*, 1984; Corma *et al.*, 1986). These reports also point out that, in acid solutions more concentrated than 1 M, the number of micro- and meso-pores decreases; the percentage of the surface area corresponding to macro-pores, relative to the overall surface area increases, and the sepiolite structure along the *c* axis collapses. This collapse shortens the fibres.

Using the second-order rate constants that were independent of the acid concentration, *i.e.*  $k'$  values calculated from the equation  $k = k' \cdot C^n$ , the activation energies estimated by the Arrhenius' Equation were found to be 14231 cal/mol for the  $\text{HNO}_3$  and 14828 cal/mol for HCl. These values are smaller than the concentration-dependent activation energy values (Gonzalez *et al.*, 1982; Gonzalez *et al.*, 1984; Corma *et al.*, 1986).

The change in the particle size of sepiolite does not effect the reaction mechanism (Fig. 3). As the particle size increases, the dissolution rate of Mg decreases due to the decreasing overall interface and increasing thickness of the layer acting as a diffusion barrier (Table 4). The increase in the average particle diameter from 0.0810 mm to 0.5020 mm causes a 50% decrease in the ratio of the  $\text{Mg}(\alpha)$  extracted into the solution within the same period.

In the experiments where the acid concentration and the temperature were kept constant, the rate constants were found to be a function of initial particle radii. To establish

a relation between the particle size and the rate constant,  $x$  and  $y$  values fitting into  $k = 2 k'/r^x$  and  $k = k'/r^y$  were calculated (Fig. 6). These parameters ( $x$  and  $y$ ) were found to be 0.5581 and 0.5583 for HCl, and 0.5113 and 0.5115 for HNO<sub>3</sub> solutions. In previous reports, no quantitative relationship between particle size and reaction rate was established; but the rate constants have been assumed to be inversely proportional to the square of the initial particle radii (Wadworth & Miller, 1979; Gonzalez *et al.*, 1982). Our results indicate that the rate constants are inversely proportional to the square-root of the initial radius.

## CONCLUSIONS

The dissolution of Mg from sepiolite is a first order reaction in terms of acid concentration and Mg content of the solid. This is confirmation that diffusion is the rate-controlling step in the dissolution reaction of Mg from sepiolite as previously suggested (Wadworth & Miller, 1979; Gonzalez *et al.*, 1982; Gonzalez *et al.*, 1984; Corma *et al.*, 1986). The tetrahedral silica sheets formed on the solid surface after the removal of Mg<sup>2+</sup> ions act as a diffusion barrier. The apparent rate constant of the dissolution process is a function of the acid concentration and the initial particle radius, and can be given as  $k = k_0 C/r^{1/2}$ .

The apparent activation energy of the dissolution reaction of Mg from sepiolite is a function of the acid concentration, and reaches a minimum of 11 kcal/mol at an acid concentration of 0.75 M for both HCl and HNO<sub>3</sub>. The activation energy of the concentration-nondependent second-order reaction was calculated to be 14.5 kcal/mol for both acids.

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