

DISSOLUTION OF HECTORITE IN INORGANIC ACIDS

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Abstract—The effect of acid type and concentration on the reaction rate and products of dissolution of hectorite in inorganic acids was investigated. The dissolution of hectorite in hydrochloric (HCl), nitric (HNO₃) and sulphuric (H₂SO₄) acids was characterized using quantitative chemical analysis, infrared (IR) and multinuclear MAS NMR spectroscopies. The rate of dissolution increased with acid concentration and decreased in the order HCl ≥ HNO₃ > H₂SO₄ at the same molar concentration. No differences were found in the reaction products of hectorite treated with the three acids. The rate of Li dissolution was slightly greater than that of Mg at lesser acid concentrations (0.25 M), indicating that protons preferentially attack Li octahedra. The gradual changes in the Si-O IR bands reflects the extent of hectorite dissolution. The analysis of ²⁹Si MAS NMR spectra relative peak intensities with dissolution time and acid concentration provided direct dissolution rates for tetrahedral (Q³) Si. After acid dissolution, most Si was bound in a three dimensional framework site (Q⁴), but a substantial part also occurred in the Si(OSi)₃OH (Q³1OH) and Si(OSi)₂(OH)₂ (Q²2OH) environments. These three sites probably occur in a hydrous amorphous silica phase. Both Al_{IV} and Al_{VI} rapidly disappeared from ²⁷Al MAS NMR spectra of the dissolution products with acid treatment. The changes in IR and MAS NMR spectra of hectorite due to acid dissolution are similar to those of montmorillonite.

Key Words—Acid Dissolution, Hectorite, IR, NMR.

INTRODUCTION

Hectorite is a trioctahedral smectite containing Mg and Li as the main octahedral cations with minor amounts of Al and Fe. Incomplete filling of all octahedral sites and heterovalent Li⁺ for Mg²⁺ substitution confers a negative charge on the octahedral sheet. The contribution of cation substitution in the tetrahedral sheets to the net negative charge is small due to very low tetrahedral substitution. Several properties of hectorite are similar to those of montmorillonite, but some differences have been reported. Jaynes et al. (1992) reported a decrease in the negative layer charge in Mg-hectorites after each of several heat treatments at 250°C, which was attributed to progressive octahedral Mg²⁺ for Li⁺ substitution. Slade et al. (1991) found that the basal spacing of hectorite expanded from 15.5 Å to 18.5 Å in NaCl solutions as the NaCl concentration decreased, corresponding to the transition from two to three sheets of water between the silicate layers. This behavior is typical of most montmorillonites. The sorption of various cations by hectorite and montmorillonite is different (Villemure 1990; Davison et al. 1991), while some Al-OH polymers had similar preferential adsorption by both (Hsu 1992). Various species, such as metal-oxide pillars and organic or organometallic complexes, have recently been incorporated into the structure of synthetic hectorites to improve the catalytic properties of the products (Luca et al. 1991;

Barrault et al. 1992; Carrado 1992; Bergaya et al. 1993).

Another method for modifying the catalytic behavior of clays is acid treatment. Reactions of clay minerals with acids are, thus widely used both in research and industry. Many industrial uses of acid treated smectites include bleaching earths (Siddiqui 1968), catalysts (Adams 1987; Breen 1991), catalyst supports (Rhodes et al. 1991; Rhodes and Brown 1992, 1993) and in carbonless copying papers (Fahn and Fenderl 1983) require study of the acid treatment processes and the properties of the products to ensure optimal performance.

The kinetics of acid reaction of clay minerals have been investigated by Osthaus (1956), Čížel and Novák (1977), Čížel et al. (1990), Luca and MacLachlan (1992) and Tkáč et al. (1994) for montmorillonites and nontronites; by Corma et al. (1987, 1990) for palygorskite; by Cetisli and Gedikbey (1990) for sepiolite; and by Gastuche and Fripiat (1962) for montmorillonite, glauconite, biotite and kaolinite. Novák and Čížel (1978) found that the dissolution rate of dioctahedral smectites in 6 M HCl increases with increasing octahedral Fe and Mg substitution. Goethite was identified as the most common readily HCl-soluble admixture in the fine fractions of bentonites (Komadel et al. 1993). Gastuche and Fripiat (1962) reported a high dissolution rate for biotite in 2 M HCl at 31°C, in spite of its collapsed structure. The reaction product of HCl-treat-

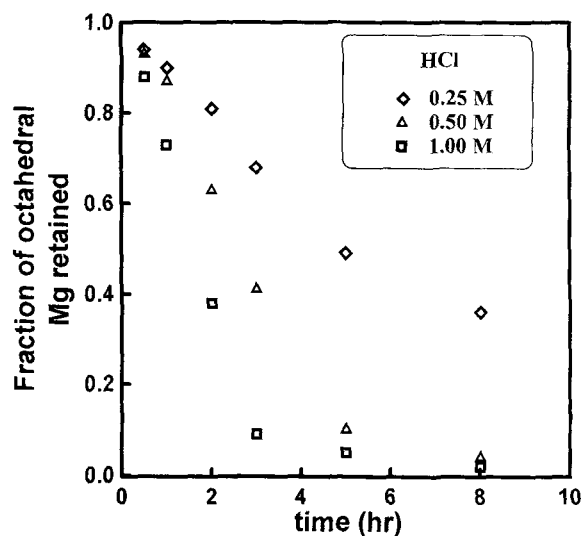


Figure 1. Undissolved fraction of octahedral Mg in hectorite after reaction with HCl at 20 °C.

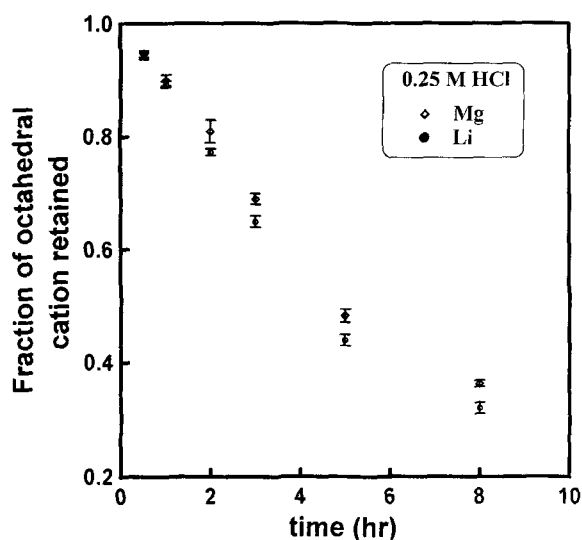


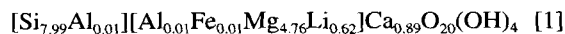
Figure 2. Undissolved fraction of octahedral Mg and Li in hectorite after reaction with 0.25 M HCl at 20 °C.

ed montmorillonite or illite/smectite is amorphous SiO_2 with a three-dimensional cross-linked SiO_4 framework containing a small amount of tetrahedral Al and about 15% of the tetrahedral Si containing one OH group (Komadel et al. 1990; Schmidt et al. 1990; Tkáč et al. 1994). The objective of this study was to determine the effect of acid type and concentration on the reaction rate and products of dissolution of hectorite in hydrochloric, nitric and sulphuric acids to understand better the acid treatment of trioctahedral smectites.

EXPERIMENTAL

Material

The hectorite (Hector, California, Ward's Natural Science Establishment, Inc.) was Ca-saturated, fractionated to less than 2 μm , washed free of excess salts, dried at 60°C and ground to pass a 0.2 mm sieve. Both X-ray powder diffraction (XRD) and infrared spectroscopy (IR) show smectite to be the primary mineral with calcite as an admixture. The total chemical composition was: 56.72% SiO_2 ; 0.15% Al_2O_3 ; 0.13% Fe_2O_3 ; 22.69% MgO ; 7.12% CaO ; 1.09% Li_2O ; and 12.13% loss on ignition. The CaO content due to calcite caused a negative coefficient for octahedral Al in the structural formula. Čičel and Komadel (1994) discussed in detail the effect of admixtures on the structural formulae of smectites. Decreasing the CaO content in the computer-fitted structural formula for hectorite yielded a distribution of CaO within the sample of 1.1% for calcite and 6.02% for hectorite. The resulting structural formula for hectorite revealed Al in both octahedral and tetrahedral sites, in accord with the ^{27}Al MAS NMR results:



Because of its high acid solubility, no admixture of calcite was identified by IR spectroscopy for any of the acid-treated samples and its effect on the results was negligible.

The possible presence of Li and Mg carbonates in non-silicate phases was checked by examining the IR spectrum of untreated hectorite, which revealed a band at approximately 1430 cm^{-1} (MgCO_3 is at 1450 cm^{-1}). No splitting of the band was detected, as is typical for Li_2CO_3 , and no shoulder was seen near 1444 cm^{-1} , which is usually present with the 1439 cm^{-1} band for dolomite (White 1974). Moreover, the extrapolations of the Li and Mg-dissolution curves (Figures 1, 2 and 3) to $t = 0$ yielded a $(1 - \alpha)$ intercept of about 1, confirming that virtually no Li or Mg was present in any readily soluble phases (Komadel et al. 1993).

Mössbauer spectroscopy of hectorite at -183°C indicated that most of the Fe is bound in non-magnetic phases, although a low intensity signal from an Fe oxide/hydroxide sextet could have been lost in the noisy background (not shown).

Acid Dissolution

For each acid dissolution reaction, a 500 mg portion of hectorite was mixed at 20°C with 100 ml of each of the following acids: 0.125 M H_2SO_4 ; 0.25, 0.5 and 1.0 M of each of H_2SO_4 , HNO_3 and HCl in a 250 ml Pyrex flask with a reflux attachment. The flask was kept in a constant temperature water bath. The mixtures were reacted, with occasional stirring, for specified times (0.25 to 8 h), filtered and washed with 300 ml water. The solid products were dried at 60°C and ground to pass through a 0.2 mm sieve. The fil-

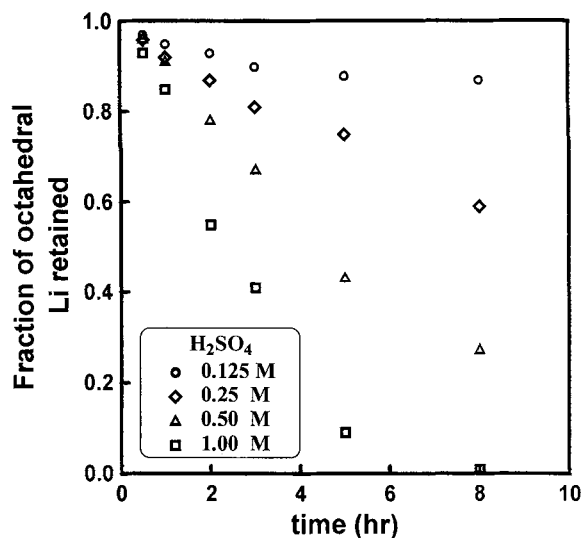


Figure 3. Undissolved fraction of octahedral Li in hectorite after reaction with H_2SO_4 at 20°C .

trate and wash supernatant solutions were combined and analyzed for Mg and Li by atomic absorption spectroscopy, yielding the amount of metal dissolved (w_t). The value of the dissolved fraction of the respective cation, α , was calculated from the relation:

$$\alpha = \frac{w_t}{w_0} \quad [2]$$

where w_0 is the total content of Mg or Li in the sample. Dissolution curves were constructed by plotting the undissolved fraction of the respective cation ($1 - \alpha$) versus time. The dissolution half-time, $t_{1/2}$, is the time required for 50% of the octahedral cations ($\alpha = 0.5$) to be dissolved and is used to compare dissolution rates (Číček and Novák 1977). To check the reproducibility of results, dissolutions in 0.25 M HCl and HNO_3 were performed in triplicate. No duplicates were measured at higher acid concentrations.

Infrared Spectroscopy

IR absorption spectra were recorded with a Perkin Elmer 983G spectrophotometer using the KBr pressed disk (13 mm dia.) technique (0.3 mg sample + 200 mg KBr).

MAS NMR Spectroscopy

Multinuclear magic angle sample-spinning nuclear magnetic resonance (MAS NMR) spectra were collected at room temperature on home-built spectrometers using probes manufactured by Doty Scientific. All powdered samples were packed into either 5 mm (Al) or 7 mm (Si) zirconia (Doty) rotors sealed with Vespel (Doty) end caps. The ^{27}Al MAS NMR spectra were collected at $B_0 = 11.7\text{T}$ (130.3 MHz Larmor frequency) with a sample spinning frequency of 9.9 kHz using radio frequency pulses of 1 μs duration and a recycle delay time of 300 ms between each successive pulse. 10,000 to 15,000 acquisitions were obtained for each spectrum. The ^{27}Al chemical shifts were referenced to external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and are reported as peak maxima. No adjustments for quadrupolar shift contributions were attempted.

The ^{29}Si MAS NMR spectra were collected at $B_0 = 8.45\text{T}$ (71.5 MHz) with a sample spinning frequency of 4.0 kHz using radio frequency pulses of 8 μs and 90 s recycle delays. Each spectrum was composed of 176 acquisitions. The ^{29}Si MAS NMR chemical shifts were referenced to tetramethylsilane ($\text{TMS-Si}(\text{CH}_3)_4$).

^1H cross polarization (CP) MAS NMR spectra for ^{29}Si were collected on a GE300WB spectrometer at $B_0 = 7.05\text{T}$ (^{29}Si Larmor frequency = 71.5 MHz, $^1\text{H} = 300\text{ MHz}$). A sample spinning frequency of 4 kHz, CP pulse of 7 μs , 2 ms contact time, and 3 s recycle delays were used for all samples. A variable contact time experiment was also performed in which the contact time ranged from 0.3 to 15.0 ms.

RESULTS AND DISCUSSION

Solution Analysis

The dissolution rates of Mg and Li depended on the acid type and concentration. For instance, the dissolved fraction of the Mg at any dissolution time increased with increasing concentration of HCl (Figure 1). After 8 h of dissolution more than 95% of the total Mg was dissolved in both 1.0 M and 0.5 M HCl, whereas only 64% of the total Mg was dissolved in 0.25 M HCl. The shape of the dissolution curves in all acids are similar for both Mg and Li (Figures 1, 2 and 3), but their relative rates varied depending on acid concentration. At the smaller acid concentrations, the rates for Li were markedly greater than for Mg in

Table 1. Half-times of dissolution ($t_{1/2}$) of Li and Mg in hectorite in acids at 20°C .

Acid mol.dm ⁻³	HCl			HNO ₃			H ₂ SO ₄			
	0.25	0.5	1.0	0.25	0.5	1.0	0.125	0.25	0.5	1.0
	----- $t_{1/2}$ (hours) -----									
Mg	4.86 ± 0.12	2.6	1.7	5.14 ± 0.17	2.9	1.8	>8	>8	4.7	2.7
Li	4.42 ± 0.08	2.5	1.6	4.74 ± 0.14	2.7	1.8	>8	>8	4.4	2.7

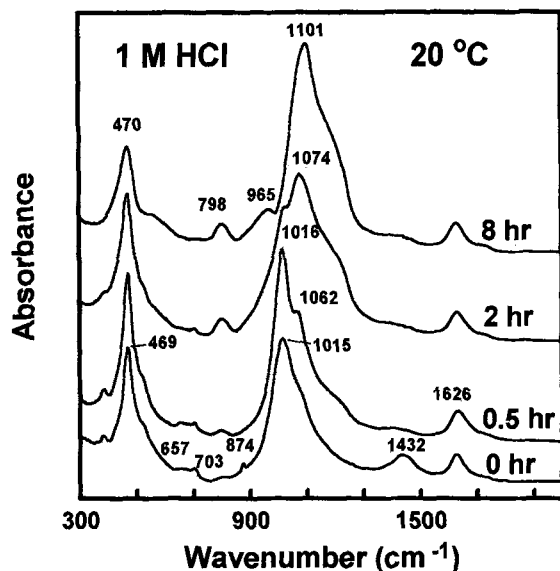


Figure 4. Infrared spectra of hectorite treated with 1 M HCl at 20 °C for different lengths of time.

all acids (Figure 2), but as the acid concentration increased, the respective dissolution rates for Li and Mg in any given acid apparently converged to a similar value (Table 1). This result indicates that at lower acid concentrations protons preferentially attacked the Li octahedra, where the local negative charge is located.

Infrared Spectroscopy

The characteristic O-H and Si-O bands (Farmer 1974) were observed in the IR spectrum of the untreated hectorite (Table 2, Figure 4, 0 hr). The OH stretching vibrations (not shown) of the $Mg_3(OH)$ unit absorb at 3675 cm^{-1} , the OH bending vibrations gave a low intensity band at 657 cm^{-1} . The main Si-O stretching band at 1015 cm^{-1} , the SiO out-of-plane bending band at 703 cm^{-1} , and the Si-O in-plane bending band at 469 cm^{-1} were also observed. The CO_3 stretching at 1432 cm^{-1} and CO_3 bending at 874 cm^{-1} are due to calcite (Figure 4, 0 hr).

Acid treatment changed several aspects of the IR spectrum of the hectorite (Figure 4). The character of these gradual, but reproducible, changes was the same for all acids studied. The most prominent of these changes were shifts in the Si-O stretching region. The Si-O stretching band at 1015 cm^{-1} diminished and the intensity of the Si-O absorption of amorphous SiO_2 near 1100 cm^{-1} (Moenke 1974) increased during the course of acid dissolution. The band at 1015 cm^{-1} is absent from the spectrum of the residue after complete dissolution of the hectorite (Figure 4, 8 hr). Further evidence for increased amorphous SiO_2 as acid dissolution progresses is also shown by the increase in intensity of the band at 798 cm^{-1} attributed to the Si-

Table 2. IR peak assignment for untreated hectorite.

Peak maxima (cm^{-1})	Assignment
3675	$Mg_3(OH)$ stretching
3427	HOH stretching
1626	HOH bending
1432	CO_3 asymmetric stretch
1070	SiO stretching out-of-plane
1015	SiO stretching in-plane
874	CO_3 bending out-of-plane
703	SiO bending out-of-plane
657	OH bending
522	MgO
469	SiO bending in-plane

O vibrations of amorphous silica (Moenke 1974). The IR spectra of dissolved hectorite residues also show a medium intensity band near 965 cm^{-1} (Figure 4, 8 hr) due to Si-O stretching of SiOH groups (Moenke 1974). The disappearance of the band at 657 cm^{-1} , assigned to bending O-H vibrations of hectorite (Farmer 1974), and the presence of only a shoulder at 1016 cm^{-1} due to Si-O vibrations in the tetrahedral sheet indicate that most of the hectorite was dissolved within the first two h of the acid treatment (Figure 4). The presence of the bands attributed to four-coordinate Si as in silica (1101 , 798 and 470 cm^{-1}) and the Si-OH band at 965 cm^{-1} (Moenke 1974), and the absence of any band attributable to hectorite (1015 , 703 and 657 cm^{-1}) in the 8-h treated sample strongly suggest that hectorite dissolution was complete (Figure 4).

The effects of acid concentration are well illustrated by the IR spectra of hectorite treated with H_2SO_4 for 5 h (Figure 5). The sample treated with $0.125\text{ M } H_2SO_4$ contained a strong absorption band at 1016

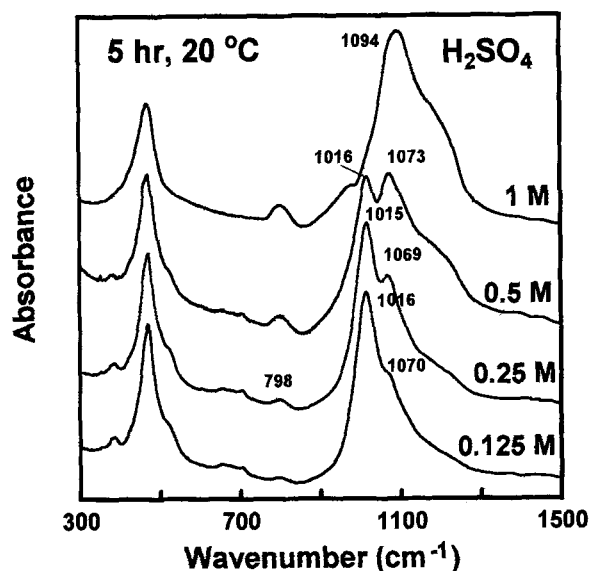


Figure 5. Infrared spectra of hectorite treated 5 h with varying concentrations of H_2SO_4 at 20 °C.

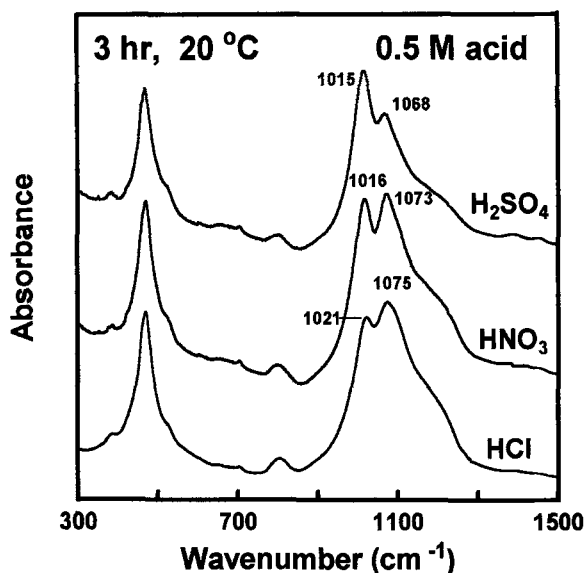


Figure 6. Infrared spectra of hectorite treated 3 h with 0.5 M HCl, HNO₃, or H₂SO₄ at 20 °C.

cm⁻¹ due to tetrahedral Si-O vibrations in the clay and only a small shoulder near 1070 cm⁻¹ due to amorphous SiO₂ (Figure 5, 0.125 M). The increased intensity of bands at 1070 and 798 cm⁻¹ (Figure 5, 0.25 M and 0.5 M), indicates a greater hectorite decomposition when treated with 0.25 or 0.5 M H₂SO₄ (Figure 3). A strong absorption at 1094 cm⁻¹ attributed to amorphous SiO₂ dominates the IR spectrum of the sample treated with 1 M H₂SO₄.

The anion of the acid also affects the dissolution rate of hectorite. At the same molar acid concentration the dissolution rate decreased in the order HCl ≥ HNO₃ > H₂SO₄ (Table 1). The role of these anions in the dissolution process is unclear, but no differences occurred in the reaction products identified from the IR spectra. For instance, samples treated for 3 h in 0.5 M acids possessed the same IR absorption bands regardless of the acid, but the intensities of the Si-O vibrations for Si in different coordination sites are different (Figure 6). The intensities of the absorption bands are proportional to the concentration of absorbing centers of the given type. The similar intensities of the tetrahedral Si-O (1016 cm⁻¹) and amorphous SiO₂ (1073 cm⁻¹) vibrations for samples treated with 0.5 M HNO₃ for 3 h indicate that about half of the hectorite was dissolved. The slightly greater intensity in the band at 1075 cm⁻¹ compared to that at 1021 cm⁻¹ (tetrahedral Si-O) for the HCl treated sample reveals a slightly greater dissolution rate in HCl than in HNO₃ (Figure 6, HCl and HNO₃). These results agree with those of the chemical analyses, which indicate that the undissolved fraction of Mg in HNO₃ was 0.49 and was 0.44 for Li in HNO₃ (Figure 2); and in HCl, 0.41 for Mg and 0.39 for Li (Figure 1). The strong

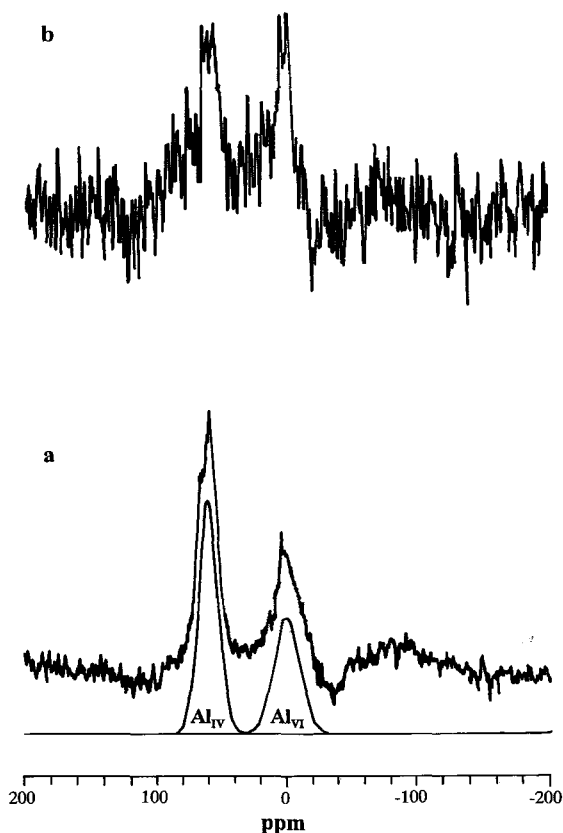


Figure 7. ²⁷Al MAS NMR spectra and peak deconvolution of hectorite treated with 1 M HCl at 20 °C for a) 0 h; and b) 3.0 h.

band at 1015 cm⁻¹ (Si-O tetrahedral) and the much weaker one at 1068 cm⁻¹ (amorphous SiO₂) for hectorite treated with H₂SO₄ (Figure 6, H₂SO₄) show less dissolution compared to HCl and HNO₃. This conclusion is further supported by the values for 1- α of 0.69 for undissolved fractions of Mg and 0.67 for undissolved fractions of Li, after 3 h in 0.5 M H₂SO₄.

The changes in IR spectra of hectorite due to acid dissolution are similar to those of montmorillonite. The dissolution of montmorillonite is assumed to be complete when vibrations attributed to octahedral cations (OH bending and Al-O-Si) disappear from the IR spectra of the residue (Komadel et al. 1990). The intensity of the OH bending vibrations of hectorite near 650 cm⁻¹, however, is too weak to use this criterion, but changes in the Si-O stretching region are more distinct and thus more useful for monitoring the dissolution of hectorite. The IR spectra of acid-dissolution residues from either hectorite (Figure 4, 8 hr) or montmorillonite (Komadel et al. 1990) have absorption bands with similar shapes and positions as a hydrous amorphous silica phase (Moenke 1974).

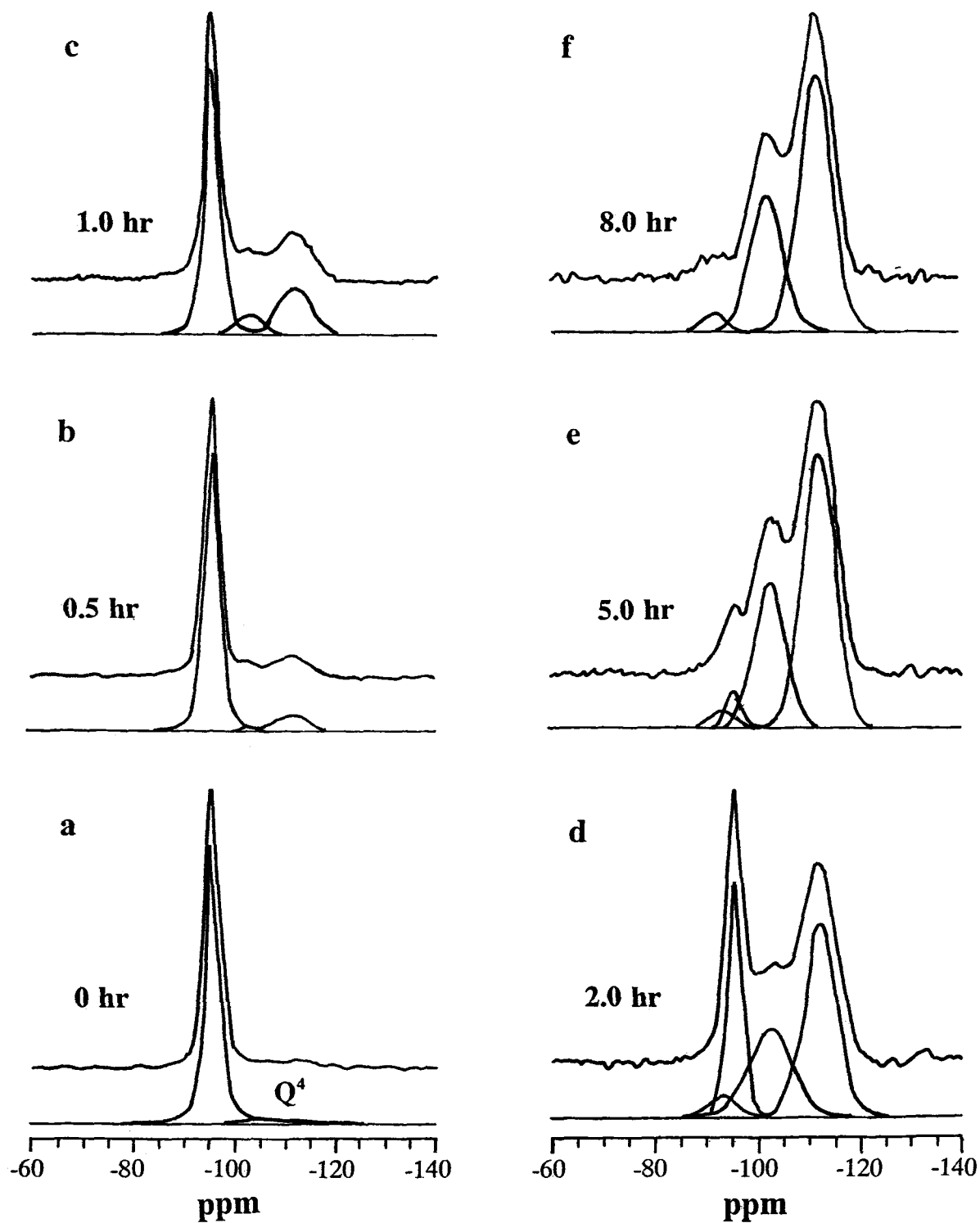


Figure 8. ^{29}Si MAS NMR spectra and peak deconvolution of hectorite treated with 1 M HCl at 20 °C for a) 0 h, b) 0.5 h, c) 1.0 h, d) 2.0 h, e) 5.0 h, and f) 8.0 h.

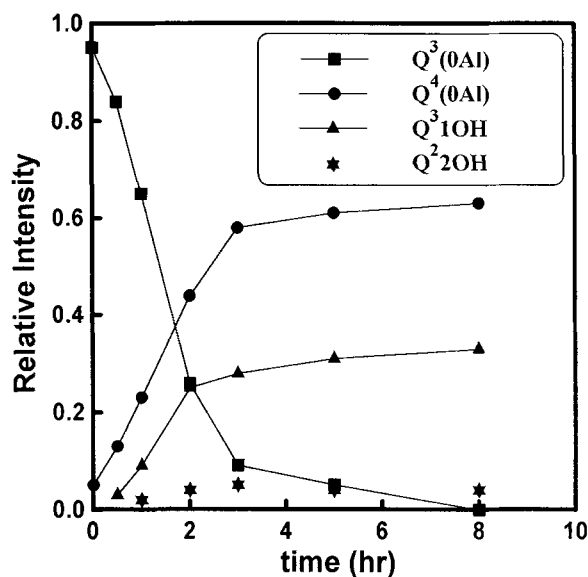


Figure 9. Effect of time of acid dissolution treatment (1 M HCl) at 20 °C on the ^{29}Si peak relative intensities for hectorite and its dissolution products.

^{27}Al MAS NMR Spectroscopy

The ^{27}Al MAS NMR spectrum of untreated hectorite reveals both tetrahedral (Al_{IV}) and octahedral (Al_{VI}) with peak maxima at 60.2 and -0.5 ppm, respectively. The relative intensity of these two peaks reveals the distribution of Al between tetrahedral and octahedral sites, which for the untreated hectorite is 60% Al_{IV} and 40% Al_{VI} (Figure 7, spectrum a). The observed chemical shifts for Al_{IV} agree with literature values from smectites with low Al substitution (Kinsey et al. 1985; Komarneni et al. 1986; Sanz and Robert 1992). The signal/noise ratio in the spectrum is poor due to the low Al content of 0.15% Al_2O_3 .

The ^{27}Al NMR signal intensity greatly decreased with acid dissolution, as illustrated by the decreased signal/noise ratio of spectrum b, Figure 7. The ^{27}Al signal of the 8 h, 1 M HCl treatment is indistinguishable from background (spectrum not shown). The loss of signal intensity and the lack of new resonances indicate that Al is lost to the solution during hectorite dissolution and is absent from the reaction products. This is in contrast with acid dissolution of montmorillonite (Tkáč et al. 1994), in which some Al_{IV} remained associated with the amorphous reaction products, but resonated at a slightly less positive chemical shift.

^{29}Si MAS NMR Spectroscopy

The untreated hectorite sample contained a strong ^{29}Si Q^3 signal centered at -95.5 ppm (Figure 8, spectrum a), in agreement with literature values for Si in low Al-substituted smectites (Kinsey et al. 1985; Ko-

marneni et al. 1986; Weiss et al. 1987; Sanz and Robert 1992). A broad, low intensity Q^4 peak occurs at -112 ppm in this spectrum, indicating the presence of a small amount of amorphous SiO_2 (Mäji et al. 1984; Engelhardt and Michel 1987).

As expected, acid dissolution resulted in redistribution of the ^{29}Si signal (Figure 8) and supports the finding from IR that similar changes occurred regardless of the acid used. Different acids affected the rate of dissolution but not the characteristics of the product. However, ^{29}Si NMR spectra provide more detailed information than IR regarding the reaction products. In addition to the Q^4 peak, two additional peaks, centered near -102 and -92 ppm, formed upon acid treatment. These peaks are due to incompletely polymerized Si sites with attached OH groups (Mäji et al. 1984; Engelhardt and Michel 1987). The signal centered near -102 ppm is assigned to $\text{Si}(\text{OSi})_3\text{OH}$ ($\text{Q}^3\text{1OH}$) sites and the signal near -92 ppm to $\text{Si}(\text{OSi})_2(\text{OH})_2$ ($\text{Q}^2\text{2OH}$) sites. Variation of the contact time in the cross polarization MAS NMR experiment with an acid treated sample (8 h, 1 M HCl) revealed an enhancement of these two peaks relative to the Q^3 (hectorite) and Q^4 peaks. The Q^4 , $\text{Q}^3\text{1OH}$, and $\text{Q}^2\text{2OH}$ sites are probably in an amorphous hydrous silica phase, as the observed spectrum is characteristic of many silica gels (Engelhardt and Michel 1987).

Upon treatment with 1 M HCl, the relative peak intensity (RI) of the Q^3 (hectorite) peak decreased, which provided another measure of the extent of dissolution (Figure 9). The rate at which the Q^3 Si peak intensity decreases in 1 M HCl is similar to the rate of disappearance of octahedral Mg (compare Figures 1 and 9). This apparent dissolution of the original hectorite is accompanied by an increase in RI of the Q^4 site, and peaks for $\text{Q}^3\text{1OH}$ and $\text{Q}^2\text{2OH}$ also emerged and increased in intensity (Figure 9). These results are comparable to those of Tkáč et al. (1994) for montmorillonite dissolution and are also in good agreement with IR spectra reported in Figure 4, as evidenced by the fact that the gradual decrease in tetrahedral Si-O (1015 cm^{-1}) and the increase in the amorphous SiO_2 (1100 cm^{-1}) IR band intensities are accompanied by corresponding changes in the Q^3 and Q^4 bands in the ^{29}Si MAS NMR spectra. The Si-OH groups of both the $\text{Q}^3\text{1OH}$ and $\text{Q}^2\text{2OH}$ sites contribute to the SiOH band at 965 cm^{-1} in the IR spectra of the 8 h 1 M HCl treatment (Figure 4, 8 hr). As much as 37% (based on peak areas in Figure 8, spectrum f) of the ^{29}Si exists in the $\text{Q}^3\text{1OH}$ or $\text{Q}^2\text{2OH}$ environments.

Acid concentration significantly affected the Si-site distribution at a given time (representative results are presented in Figure 10) and agrees well with the IR results (Figure 5). The Q^3 (hectorite) RI decreased linearly with increasing acid concentration, whereas the RI of the Q^4 and $\text{Q}^3\text{1OH}$ peaks increased linearly. The RI of the $\text{Q}^2\text{2OH}$ peaks increased up to the 0.5 M

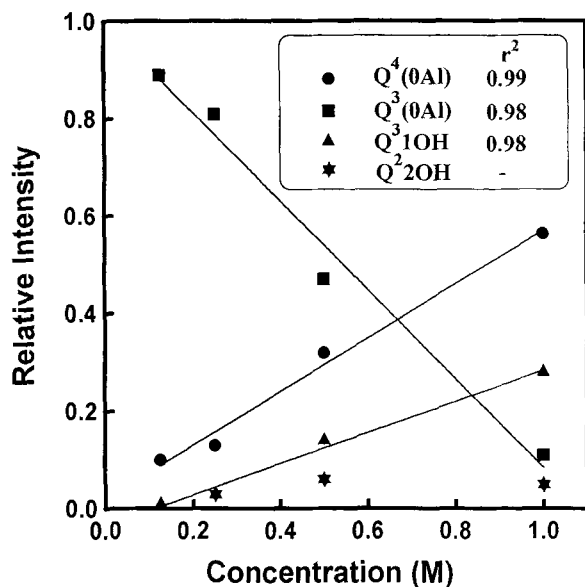


Figure 10. Effect of acid concentration (5.0 h, H₂SO₄) at 20 °C on the ²⁹Si peak relative intensities of hectorite and its dissolution products.

H₂SO₄ treatment, and then remained constant. At 5 h, the 0.5 M H₂SO₄ treatment resulted in substantially less hectorite dissolution than the 1 M HCl treatment (compare Figures 5 and 10). The HCl treatment dissolved more than 95% (Figure 1), whereas the H₂SO₄ treatment dissolved at 52% (Figure 10) of the Q³ of the initial hectorite present.

CONCLUSIONS

²⁷Al MAS NMR showed that the small amount of Al present in hectorite occurs as both Al_{IV} and Al_{VI} and that neither detectable Al_{IV} or Al_{VI} occur in the reaction products of acid dissolution. The rate of hectorite dissolution, as determined from residual Mg and Li, increased with acid concentration; and at the same molar acid concentration, the dissolution rate decreased in the order HCl ≥ HNO₃ > H₂SO₄. Lithium dissolved slightly faster than Mg at acid concentrations less than 0.5 M, which may indicate that protons preferentially attack Li octahedra, consistent with their greater negative charge compared to Mg octahedra.

Relative intensities of the Si-O stretching bands of hectorite near 1015 cm⁻¹ and of amorphous silica near 1100 cm⁻¹, provide direct information on dissolution of the mineral. Analysis of changes in the relative peak intensities of ²⁹Si MAS NMR spectra with time of dissolution, and acid concentration, provides direct dissolution rate data and reveals that the hectorite dissolution rate was higher in HCl than in equal-molar H₂SO₄, consistent with IR spectroscopy and solution Li and Mg concentrations. Si is bound in the reaction product as hydrous amorphous silica containing Q⁴,

Q³1OH, and Q²2OH environments. The changes in IR and ²⁹Si MAS NMR spectra of hectorite due to acid dissolution are similar to those of montmorillonite. A combination of these spectroscopies is extremely useful to probe structural changes that occur during the acid dissolution process of smectites.

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